H I L G A R D I A

A Journal of Agricultural Science Published by the California Agricultural Experiment Station

VOL. 12 | FEBRUARY, 1939 | No. 5

THE USE OF CHEMICAL DATA IN THE PROGNOSIS OF PHOSPHATE DEFICIENCY IN SOILS[1,2]

JOHN S. BURD[3] AND H. F. MURPHY[4]

LACK OF CORRELATION BETWEEN PLANT GROWTH AND ACID-EXTRACTABLE PHOSPHATE

SOIL CHEMISTS have long recognized that there is a certain rationale in extracting soils with acids to determine the capacity of soil particles for releasing ions to the plant. Unfortunately, attempts to correlate the actual amounts of given ions released by acids in the laboratory with the amounts of such ions absorbed by plants have not been highly successful.

Two general types of explanation might account for the discrepancy. The first of these is that, although the release of H ion to the soil by plants and microörganisms is always quantitatively important, the plant can, by absorbing from the liquid phase, shift the equilibrium between the liquid and solid phase without a material change in the H ion concentration of the system. Ions thus released independently of evolution of acid by the plant become a part of the soil solution and can be absorbed by the plant. Moreover, H. Jenny[5] has shown that the merging of the swarm of ions in the electrical double layer of the soil particle with a similar system at the root-hair surface, is sufficient to cause the removal of an exchangeable cation from the soil to the root hair and that there is no necessity for postulating the presence of a discrete intervening layer

[1] Received for publication June 15, 1938.

[2] This paper was written by the senior author and is based upon experiments formulated in conference by both authors. The experimental work was performed by the junior author.

[3] Professor of Plant Nutrition, University of California.

[4] Graduate student, University of California 1930–31 and 1937–38; now Associate Professor of Soils, Oklahoma Agricultural and Mechanical College.

[5] Unpublished data.

of soil solution or the excretion of acids by the plant to account for acquisition of such ions by plants. We suggest that this type of exchange could also take place if the soil particles and root-hair surfaces carry mutually exchangeable anions. That such exchanges may occur, but to widely varying degrees, in practically all soils is extremely probable. Such exchanges could dominate in soils whose colloidal particles approach saturation for particular ions and are in contact with kinds of root surfaces which are likewise highly saturated with ions of appropriate sign of charge (+ or —). This latter condition might be met by some kinds of plant root surfaces and not by others; thus the superior acquisitive power of certain plants for certain ions (for example, rye for phosphate) might be accounted for.

The second type of causes of failure to obtain correlations between acid extractions and growth or absorption (on the part of the plant) is largely of a technical character.

Several causes are rather obvious. Thus, the larger *amounts* of acid solutions necessarily used in the laboratory treatments exceed the buffering capacity of the soil; they produce greater shifts in H ion concentration, and dissolve larger amounts of a given ion—for example, phosphate—than would be likely to dissolve in the field. Moreover, the relative amounts of a given ion extracted from different soils by acid vary with the amounts of acid used and with the magnitude of the shift in H ion in the equilibrium solutions produced by equal amounts of acid.

A good illustration of this is afforded by data previously reported from this laboratory (*8*):[6] Two soils of similar physical properties and approximately equal pH were treated with varied amounts of acid and the soils subjected to displacement in the manner usual in this laboratory (*1*). When the amount of acid was theoretically equivalent to 1/24 *N*, the first soil shifted the pH of the displaced solution to 5.9, the second to 6.6. The amounts of phosphate brought into solution were 29.5 mg and 5.0 mg respectively, a ratio of 6 to 1.

In a comparative experiment with acid applications equivalent to 4/24 *N*, the first soil shifted the pH of the displaced solution to 4.5, the second to 6.2; and the amounts of PO_4 were 67.6 mg and 6.0 mg respectively, a ratio of 11 to 1.

Again, using the same data, if the results are studied on the basis of the shift in pH instead of amount of added acid, at pH 6.5 the amounts of PO_4 brought into solution were 11.0 mg and 6.0 mg, respectively, or a ratio of about 2 to 1. At pH 5.5, the amounts of PO_4 were 55.0 mg and 3.0 mg respectively (an actual decline from that at pH 6.5), or a ratio

[6] Italic numbers in parentheses refer to "Literature Cited" at the end of this paper.

of 18 to 1. Thus, if the figures are used to show the relative differences in supplying power of the two soils, the relation would be:

{ 6 to 1 for small amounts of acid
{ 11 to 1 for larger amounts of acid
or
{ 2 to 1 for one increment of shift in pH
{ 18 to 1 for another increment of shift in pH

These discrepancies are due to the fact that the acid comes in contact with different kinds of particles, and ions released by one kind of particle or compound become subject to secondary reactions. In the field, on the other hand, individual root hairs may influence solution from individual particles and the plant can remove dissolved substances before they have opportunity to react with other types of soil particles, or compounds, or with the free ions in the soil solution. This is also well illustrated by the work referred to above. Thus, it was shown that one of the effects of increasing acidity in a series of equilibrium treatments is to dissolve calcium or other ions, which in turn precipitate phosphate. Thus the phosphate figures so obtained do not reflect the magnitude of the effect of acid produced by H ion at the interphase boundary between a single particle and a root hair.

The effects of the type of secondary reactions (chemical and mass-action effects) just referred to, are now generally recognized and must, of course, be taken into account in interpreting data derived from the acid treatment of soil. It would, however, be unsafe and even absurd to conclude that this type of secondary reaction (precipitation) is the exclusive cause of the removal of phosphate from acid extracts. Many workers[7] have observed that various soil and colloidal clay minerals have great capacity to remove PO_4 from solutions and have ascribed this to an adsorption. Some of the data reported are, unfortunately, subject to the criticism that release of Ca ion by exchange with H ion could have caused the precipitation of phosphate and thus vitiated the conclusion that the effect is an adsorption phenomenon.

A notable attempt to elucidate the rôle of adsorption in phosphate fixation was that of Russell and Prescott (*7*). These investigators were unfortunate in that their experiments were performed at a time when the importance of the secondary chemical reactions discussed above were not generally recognized. Moreover, their conclusions were largely based on adsorption isotherms conforming to the Freundlich equation. Comber (*2*) pointed out the possibility of chemical reactions, and Fisher (*3*) showed the inadequacy of conformity to the Freundlich equation

[7] See the bibliography in Murphy (*5*).

as the exclusive test of an adsorption. These criticisms of the conclusions from the particular experiments are, of course, valid, but they do not prove that adsorption may not have played a part in determining the actual experimental results. Whether complexes capable of adsorbing phosphate were present in substantial amounts in these particular soils is perhaps of no general interest at this late date. The point is that an overemphasis of the rôle of secondary chemical reactions, important as these are in many soil types, has prejudiced the interpretation of data from experiments with phosphate in which the secondary reactions may have been caused by adsorption or exchange.

Murphy (*5*), in the accompanying paper, shows that a certain soil (Aiken clay loam), in which the colloidal clay component was largely of the kaolinitic type (as shown by X-ray diffraction photographs), reacted under experiment in the same manner as would have been expected from the studies of finely ground kaolinite carried on concurrently. In experiments with kaolinite, the material manifested the usual properties of colloidal alumino-silicates characterized by a low silica : alumina ratio. The kaolinite removed cations (K) most effectively from alkaline solutions and anions (PO_4) from acid solutions. The absence of ions capable of precipitating PO_4 precludes any other explanation than that of an adsorption. The similar behavior of the soil definitely points to its natural kaolinite component and to an adsorption reaction as the cause of the negligible amounts of phosphate removed from the soil by acid. Crops planted on the soil manifest all the symptoms of phosphate deficiency and the soil is practically immune to phosphate fertilization except when the applications are beyond economic possibility or where the fertilizer is localized in immediate contact with the absorbing roots. Phosphate adsorbed by this soil (and by the kaolinite) is not brought into solution except to a negligible extent by acid until the amount of acid is sufficient to shift the reaction of the equilibrium solution to about pH 1.0 when the aluminum silicates are breaking down, as demonstrated by the copious solution of Al and the release of soluble and colloidal SiO_2.

The paper in which these results are reported (*5*) also demonstrates a substantial phosphate-adsorbing capacity for other types of clay minerals (Volclay and bentonite). The much greater adsorbing capacity of kaolinite depends on its being finely ground. Even when finely ground, however, the kaolinite particles are probably much coarser than the particles of Volclay and bentonite as shown by the physical properties of liquid mixtures, ease of filtration, etc. The clays with high silica : alumina ratio are highly dispersed in water and are probably in a very fine state of subdivision in most soils. The kaolinite in natural soils (*6*) appears to

vary more in particle size than other clay minerals, and phosphate-adsorbing capacity of kaolinitic soils must therefore vary widely, even between soils of equal kaolinite content.

It is obviously impossible to devise a technique yielding index figures that can be applied with exactness to express the acid solubility of phosphate from the *individual* phosphate-carrying particles of the soil. With the vast majority of arable soils, a variable proportion of the phosphate rendered labile (dissolved) by acid is precipitated or adsorbed. Fairly good correlations between acid-soluble phosphate of soils and the phosphate-fertilizer requirement of plants are sometimes claimed. Such correlations must, however, be limited to slightly buffered soils, containing only small amounts of adsorbing clay minerals or clay minerals of low specific adsorbing capacity or clay minerals which are nearly saturated with phosphate.

The preceding discussion of data on or conclusions from acid extractions of soils concerned equilibrium extractions with "strong" acid (HCl). Many suppose, however, that the use of "weak" acids remedies some of the defects pointed out above.

The use of buffered acids, of course, prevents the rise of H ion concentration in the equilibrium solution and eliminates the secondary chemical precipitations, which tend to lower the phosphate figures actually obtained by use of unbuffered acid. In the field, however, the H ion concentration about an individual phosphate-carrying particle would rise greatly or little, as a result of CO_2 excretion by the plant, according to the distance of the particles of potentially soluble neutralizers, such as $CaCO_3$ or Ca-clays, from the phosphate-carrying particle. Thus, if the neutralizing power of a given soil is primarily due to $CaCO_3$, the amount of phosphate in solution at any one time in the field, as a result of acid excretion by plants, would depend upon the size and distribution of the $CaCO_3$ particles. In the laboratory at equilibrium, however, the phosphate dissolved by acid would be primarily a function of the total amount of $CaCO_3$.

Perhaps the most unfortunate occurrence in the history of soil-phosphate investigation was the choice of citric acid as a solvent. Dilute solutions of citric acid *do not dissolve* phosphate from the adsorption complex of soils: the citrate anion *displaces* phosphate from the adsorption complex.

But the plant cannot do this unless it excretes citrate ion, OH ion, or some other ion which is highly adsorbed by the clay complex, or by hydrogels when these are involved. Possibly some plants excrete enough organic acids containing anions which are strongly adsorbed. This spe-

cial ability could account for a relatively greater power of such plants to acquire phosphate from a given adsorption complex. Even if some plants could be shown to do this to a considerable degree, even if the contact phenomenon emphasized by Jenny is accepted *in toto,* it is certain that plants in general acquire adsorbed phosphate with great difficulty unless the individual particles are highly saturated (*9*) and the number of such particles is great.

We hesitate to use the term "availability," but in the sense in which this term is commonly applied, the phosphate contained in clay minerals is only slightly available,[8] while that removed by *dissolving* phosphates is extremely available, unless prevented from dissolving by a high buffer power on the part of the soil.

Thus, two soils extracted with citric acid could give equal and relatively large amounts of phosphate (as compared with the great majority of soils), and yet be very different in phosphate-fertilizer requirements. If in one soil, the phosphate in the citric-acid extract were actually derived from solution of phosphate, probably no fertilizer would be required. If, however, the phosphate in the acid extract were derived from an adsorption complex, a need for fertilization would almost certainly be indicated for most plants.

A simple experiment reveals all the facts necessary to the above conclusion. Finely ground kaolinite was partially saturated with phosphate. Five-gram portions, containing 61.45 mg PO_4, were brought to equilibrium with the respective solutions as noted. The following amounts of PO_4 were removed at equilibrium (1:5 suspensions), out of a possible 61.45 mg:

	pH value	PO_4 removed, mg
0.1 *N* Citric acid	2.27	21.88
0.005 *N* Hydrochloric acid	2.28	1.00
0.1 *N* Hydrochloric acid	1.01	6.84
0.1 *N* Sodium hydroxide	12.00	50.00

Hydrochloric acid (0.1 *N*) dissolves Al from kaolinite and releases small amounts of phosphate. Phosphate is *not displaced* from the adsorbed condition by hydrochloric acid of any pH short of one which breaks down the alumino-silicates of the adsorbing complex. In the pH range possible about an individual particle of clay complex in normal soils, there is no release of adsorbed phosphate as a result of a specific "acid" effect. Under such circumstances, phosphate is released only if the acid is one with a strongly adsorbed anion.

[8] Unless the particles are highly saturated and the *amounts* of phosphate so held are large.

FACTORS AFFECTING PHOSPHATE AVAILABILITY

From the preceding analysis, we suggest that the points to be determined in laboratory studies of soils in order to predict the need for phosphate fertilizers are as follows:

1. The amounts of phosphate liberated by acids of a type whose anion is not adsorbed by clay minerals or Fe hydrogels.[9]
2. The shift in pH caused by added acid, because this indicates whether increased acidity in the field would or would not be likely to shift the pH enough to cause the solution of phosphate to the extent observed in the laboratory.
3. The degree of phosphate saturation of the adsorbing clay minerals or adsorbing hydrogels.
4. The total phosphate (fusion analysis of the soil).

We now present for analysis the results of a series of experiments with a single soil, carried out in such a manner as to differentiate between precipitation and adsorption effects. All data represent 1:5 equilibrium extracts of 100 grams of a fine sandy loam soil (known as No. 117 in this laboratory) with amounts of acid (or alkali) producing the pH values noted at equilibrium. Series of extracts were made on the soil alone, soil + excess $CaCO_3$, soil + 400 mg Ca as $CaCl_2$, soil + 1 gram finely ground kaolinite.[10] The soil was chosen as one having no kaolinite and having little buffering power according to standards accepted for soils of this region. The soil does contain other clay minerals, and undoubtedly some of its phosphate is held as adsorbed phosphate. Moreover, the exchange complex does release calcium on acid treatment but not nearly so much as highly buffered soils of this region. When such a soil is extracted with dilute HCl, the resulting figures represent the amount of phosphate derived from solution of individual phosphate-carrying particles minus the phosphate precipitated or adsorbed.

The points on the curve representing the acid side of neutrality (see curve *A*, fig. 1) are obviously lower than they would have been if the phosphate-carrying particles could have been isolated and these alone extracted. This cannot be done, and calculations of the magnitude of this depressive effect from calcium released or amount of clay present are of little value because of the complexity of the equilibrium solution and lack of knowledge of the amounts of each clay mineral and the specific adsorbing capacity of each such mineral in this particular soil.

The curve (curve *A*, fig. 1) can, however, be analyzed and the dominating factors which determine it characterized. If the data are plotted in

[9] Possibly Al hydrogels in some soils at certain pH values.

[10] Data not presented for soil + excess $CaCO_3$. All acid treatments with $CaCO_3$ in excess, gave about equal pH values and equal phosphate figures.

absolute terms (curve *A*, fig. 2), the curve is practically a straight line on the acid side in the H ion range between pH 5.17 and 3.65. The slight change in the slope of the line at the lower pH values can be accounted for either by a small amount of precipitation or by adsorption effects or by both. The straightness of the line, however, indicates that the major effect is solution of phosphate-carrying particles or compounds. On the alkaline side (curve *B*, fig. 2), the curve is apparently logarithmic and

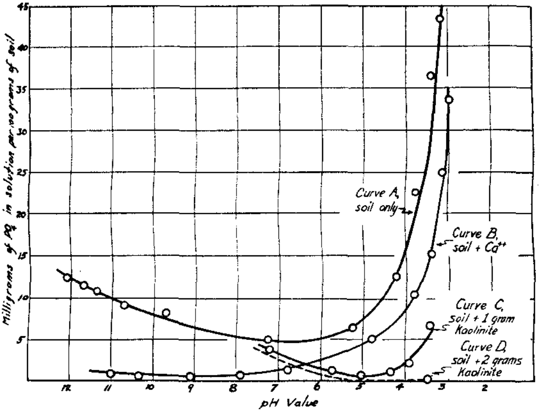

Fig. 1.—Phosphate determined in 1:5 equilibrium extracts from a variously treated slightly buffered soil, by acid and by alkali. Concentrations of HCl and NaOH used were *0.002, 0.004, 0.006, 0.008,* and *0.010 N.* The data for the kaolinite treatment on the alkaline side were essentially the same as for the untreated soil and are omitted to avoid confusion of the lines.

can be shown (if plotted logarithmically) to obey the Freundlich equation. All of the common phosphate compounds, which do not hydrolyze, become less and less soluble with increasing alkalinity. The rise observable with increasing alkalinity could be due to hydrolysis of iron, aluminum, or manganese phosphates (*8*); or to exchange of OH with PO_4 adsorbed either by clay minerals or by iron or aluminum hydrogels (*5*). As a matter of fact, an exchange of OH for the PO_4 of the clay minerals is undoubtedly the cause of the increase in this particular soil, but it really does not matter because all three classes (clay minerals, hydrogels,

and iron or aluminum phosphate) of phosphate complex would act in the same manner with OH.

As may be seen from curve *B* of figure 1, addition of 400 mg Ca ion as $CaCl_2$ to 100 grams of soil depressed the solubility of phosphate throughout the entire range. On the alkaline side, the PO_4 released from the soil minerals by OH exchange is almost completely precipitated by a very

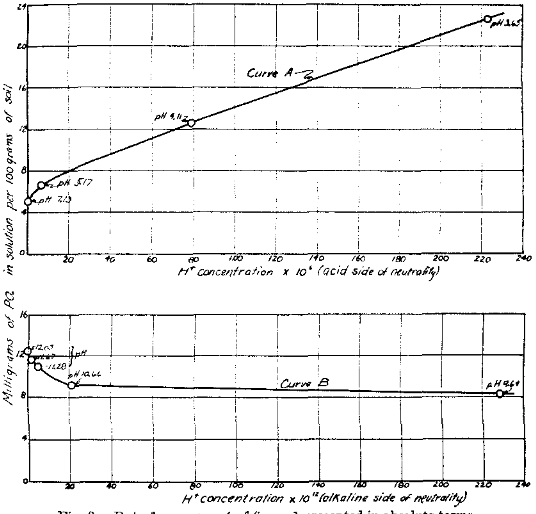

Fig. 2.—Data from curve *A* of figure 1 presented in absolute terms.

small application of Ca ion. In the soil alone (curve *A*, fig. 1) there was not enough dissolved calcium (that is, Ca ion) at pH values above 7 to produce this effect; the phosphate released from the soil minerals therefore remained in solution as determined.

As may be seen from curve *C*, figure 1, 1 gram of kaolinite in 100 grams of soil removes a large proportion of the PO_4 released by acid, the adsorption increasing with increasing H ion (decreasing pH) at first, but later rising. This latter rise is evidently due to the fact that, at the lower pH values, the clay mineral is approaching saturation. That this is so is

shown (curve *D*, fig. 1) by the supplementary experiment: 2 grams of kaolinite removes all of the phosphate released by acid. *Evidently then, the degree of saturation and the amount* of adsorbing clay minerals in a soil is what determines their ability to conceal the true acid solubility of soil phosphate. Moreover, the degree of saturation of the clay mineral particles and the number of those particles in immediate contact with potentially acid-soluble phosphate particles must determine the amount of phosphate that is actually dissolved in the soil by biologically produced acids. If the clay minerals are only *slightly* saturated with phosphate and very numerous as compared with other phosphate-carrying particles, the excretion of acids by the plant will merely move the phosphate from the acid-soluble particles to the practically insoluble adsorption complex. If the plant gets phosphate from this complex, it does so, not by acid solution, but as a result of exchanges, as suggested by Jenny for cations. Here again, the amount of phosphate the plant can get from the adsorption complex is determined by degree of saturation and amount of adsorbed phosphate.

An interesting point is whether any factor other than pH in the complex mixture of ions in the acid extracts has any effect upon the adsorbing capacity of the clay minerals. At pH 3.6, the amount of phosphate released by the soil was 23.5 mg (curve *A*, fig. 1). The amount of phosphate *not* removed by the kaolinite was 3.4 mg (curve *C*). The kaolinite had, therefore, adsorbed 20.1 mg and was in equilibrium with a solution containing 3.4 mg. We, accordingly, made up a number of solutions, all containing 23.5 mg of PO_4 (from KH_2PO_4) in 500 cc, after adjusting the H ion concentration to give values of about pH 3.6 when 500 cc of solution was brought to equilibrium with 1 gram of kaolinite. One of these equilibrium mixtures, with a pH of 3.69, had approximately the same PO_4 *ion* content as the soil-kaolin-acid mixture, as shown below:

Equilibrium mixture	pH	Phosphate adsorbed, mg	Phosphate in solution, mg	Total phosphate, mg
100 grams soil + 1 gram kaolinite + 500 cc dilute HCl....	3.60	20.1	3.4	23.5
1 gram kaolinite + 500 cc dilute KH_2PO_4 solution..............	3.69	19.3	4.2	23.5

The distribution of phosphate between kaolinite and solution is essentially the same in the two mixtures, which are otherwise very different. Apparently the only factors which affect the phosphate-adsorbing capacity of the clay minerals are PO_4 concentration and pH.

INFORMATION REQUIRED TO DIAGNOSE PHOSPHATE DEFICIENCY

In the preceding discussion, the points emphasized are the importance of determining the degree of saturation of the adsorbing complexes (minerals, hydrogels, etc.); the specific capacity of potentially soluble phosphate particles to dissolve in acid; the effect of buffers (Ca ion, etc.) in lowering the apparent solubility of these particles; and the total phosphate content of the soils. How are these factors to be determined, and how can they be evaluated?

The degree of saturation of the adsorbing constituents of the soil can be readily calculated if the amount of adsorbed phosphate actually present in the soil is known, together with the amount of phosphate the adsorbing minerals *could* hold at saturation, that is, the adsorption capacity. These figures can be ascertained from 0.1 *N* NaOH equilibrium extracts[11] of the soil itself and of the soil *after* saturation with PO_4. The actual concentration of the NaOH is not important provided it is uniform for both treatments, is sufficiently concentrated to overcome buffering on the alkaline side of neutrality, and produces a high pH in the equilibrium solution.

The adsorption capacity of an adsorption complex is, of course, affected by the pH at which the adsorption takes place (and the concentration of phosphate in the treating solution), but if concentrated solutions of KH_2PO_4 at pH 4.5 are used in the proportion of 500 cc to 100 grams of soil, the pH of the equilibrium solution will usually lie between 4.5 and 7.0 and the absolute amounts adsorbed will not vary greatly. Moreover, in those soils in which adsorption effects are important, the adsorbing capacity for PO_4 is very great as compared with the amounts actually in the adsorbed condition; so that a considerable variation in the determined adsorption capacity could not materially affect the calculated values of what we call the "degree of saturation," or the "adsorption deficit."

The specific capacity of phosphate-carrying particles to dissolve in acids cannot be determined exactly except in soils having no buffer capacity and which are also free from adsorbing complexes. The general order of magnitude of this factor can, however, be inferred from the amounts of phosphate extracted by acid and the determined buffer capacity of the soil. Five volumes of 0.01 *N* HCl to 1 gram of soil will shift the pH more than any plant could do, but not enough to overcome the buffering

[11] Equilibrium extracts do not give the entire amount of adsorbed phosphate, but they give almost all, and all that need be considered in these relations.

power of soils. The shift in pH actually observed by this treatment gives an appropriate measure of the buffer capacity of the soil.

The determination of total phosphate by fusion analysis presents no difficulty. This datum is necessary to give weight to the quantity factor, in supplementing conclusions drawn from the data showing the degree of saturation.

APPLICATION OF CHEMICAL DATA TO PROGNOSIS OF PHYSIOLOGICAL PHOSPHATE DEFICIENCY

The evaluation of the criteria suggested will obviously depend upon comparisons between the known physiological responses to phosphate fertilization of individual soils, and the figures or indexes obtained from such soils by the methods outlined.

This we believe we have accomplished for a group of fourteen soils of widely different characters. The minor defects of our correlations are apparently due to the incompleteness of the physiological data and to variation in the specific capacity of different plants to acquire phosphate from particles of equal degree of saturation. The first defect can be overcome by obtaining further evidence of physiological deficiency in the particular soils. The second defect can never be entirely eliminated, but its elimination is not necessary if the data are not interpreted too narrowly. Fertilizers are not so valuable that the most effective dosage must be predicted with a high degree of accuracy. To be able to say that for the generality of crops such and such a soil will probably respond to phosphate applications, is sufficient.

Many of the soils used in these experiments are the same as those used by Hibbard (*4*), who gives additional data on them.

Phosphate-deficient Soils.—By referring to table 1, the reasons why the soils manifesting great phosphate deficiency are unable to supply the plant are perfectly obvious. Soils 103, 69A, and 64 yield practically no acid-soluble phosphate: their unsatisfied adsorption capacity is so great (adsorption indexes, 3.28, 1.54, and 0.93) as compared with their phosphate content, and the degree of saturation is so small that the adsorption complex holds phosphate with great avidity, and the plant cannot easily remove it.

Soil 78 can yield practically no acid-soluble phosphate; this is definitely referable to its high adsorption index. The degree of saturation is high and individual particles of adsorption complex could be expected to yield phosphate well to the plant, but the low total phosphate, the effect of which is reflected in adsorption index, prevents plants from getting phosphate rapidly.

TABLE 1

CHEMICAL DATA (PO_4) FROM SOILS OF KNOWN PHYSIOLOGICAL RESPONSE

Soil No. and *description*	PO_4 per 100 grams of soil: Adsorption capacity*	PO_4 per 100 grams of soil: *In adsorbed condition*†	Present degree of *saturation* (col. 1 / col. 2)	PO_4 per 100 grams of soil: Adsorption deficit (col. 1 − col. 2)	PO_4 per 100 grams of soil: Total‡	Adsorption index (col. 4 / col. 5)	PO_4 per 100 grams soil, acid-soluble§	pH of acid equilibrium	Mineral characteristics¶	Buffering ability	Phosphate deficiency indicated by plant growth
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*
	mg	*mg*	*per cent*	*mg*	*mg*		*mg*	*pH*			
103. Aikin clay	547	22.0	4	525	160	3.28	0.2	4.78	Kaolinite	Moderate	Extreme
69A. Sites clay loam	290	44.0	15	246	160	1.54	0.8	3.89	Kaolinite	Moderate	Great: extreme for tomatoes, etc., but not for fruit trees
78. Fine sandy loam	105	30.4	29	75	45	1.67	1.2	2.74	Kaolinite and montmorillonite	Slight	Great: extreme for tomatoes; moderate for barley; none for fruit trees
64. Vina silt loam	174	16.4	9	158	170	0.93	0.6	4.81	Kaolinite	Moderate	Great: marked for tomatoes; moderate for alfalfa
38. Vina silty clay loam	181	23.6	13	157	250	0.63	4.8	5.22	Kaolinite	Substantial	Intermediate: none for some time
36. Farwell sandy loam	126	13.6	11	112	250	0.45	1.9	6.19	Kaolinite and montmorillonite	Substantial	Intermediate: marked for tomatoes
40. Altamont-Olympic-loam wash	172	41.6	24	130	330	0.39	13.4	4.86	Mineral X and montmorillonite	Moderate	None
37. Nord sandy loam	51	10.4	20	40	240	0.17	5.5	8.50	Faintly kaolinite	Extreme	Intermediate: moderate for tomatoes, much less than No. 36 at first
1C. Yolo silty clay loam	55	26.6	48	28	200	0.14	5.1	7.09	Montmorillonite	Substantial	None
68A. Tujunga fine sand	23	4.4	19	19	140	0.14	17.9	3.50	....	Slight	Unknown, no information
53. Delhi sand	29	18.0	62	11	80	0.14	46.7	2.86	....	Slight	None for first crop; later marked for tomatoes
30. Fresno fine sandy loam	32	6.0	19	26	160	0.16	40.6	3.00	....	Slight	None for some time; after several crops, moderate for tomatoes
75. Yolo loam	87	12.8	15	74	232	0.32	9.1	6.25	Montmorillonite	Substantial	None
80. Hanford fine sandy loam	8	4.4	55	4	115	0.04	0.6	7.75	Mineral X	Extreme	Great: very marked for tomatoes; largely corrected by making soil acid

* The adsorption capacity represents the phosphate removed by 0.1 *N* NaOH (1:5, 1-hour equilibrium suspensions); from soil subjected for 15 hours to a KH_2PO_4 solution (1:5) containing approximately 3 mg of PO_4 per cc and having a pH of 4.5. The free KH_2PO_4 present in the soil was leached out with distilled water before applying the NaOH treatment.

† Direct determination on soil—0.1 *N* NaOH (1:5) 1-hour equilibrium syspension.

‡ Fusion analyses.

§ Determined from a 24-hour equilibrium suspension of soil and 0.01 *N* HCl (1:5).

¶ Determined from X-ray photographs.

Soil 80 has a negligible adsorption deficit and negligible amounts of adsorbed phosphate. Plants suffer because the potentially acid-soluble phosphate is prevented from coming into solution as a result of the high buffer capacity of the soil.

Soils of Intermediate Phosphate-supplying Power.—Of this group, soil 36 shows early physiological deficiency. Soils 37 and 38 show deficiency in subsequent crops. Soil 36 yields very little acid-soluble phosphate, primarily owing to its substantial buffering capacity, aided by a substantial capacity to adsorb phosphate (adsorption capacity 126, adsorption index 0.45). In soils 37 and 38, the amounts of acid-soluble phosphate are greater than for No. 36 but are not large, owing entirely to buffering in soil 37 and primarily to adsorption in soil 38. The buffering of No. 37 is capable of being remedied by (acidic) applications in the field, but the acid-soluble phosphate of No. 38 should decline under cropping, as indicated by the high adsorption index (0.63).

Soils of Good Present Supplying Power.—The lack of present physiological deficiency for plants in soils 40, 53, and 30 is easily accounted for by the comparatively large figures for acid-soluble phosphate. The relatively lower acid-soluble figure of No. 40 as compared with Nos. 53 and 30 is referable to the higher adsorption index (0.39 as against 0.14 and 0.16); inasmuch as the soil is only moderately buffered.

Soils 30 and 53 both manifest phosphate deficiency after a relatively small number of crops have been grown. This cannot be explained on the basis of a transfer of potentially acid-soluble phosphates to the adsorption complex, for the adsorption indexes are low; it must be otherwise accounted for. This we believe can be done as follows: The very high figures for acid solubility (*in vitro*) reflect a high acid solubility for both the soils. The buffering power of both of these soils is negligible, so that their individual phosphate-carrying particles could not be prevented from delivering PO_4 to the soil solution with normal CO_2 excretion by plants. This means a concentrated soil solution, with respect to phosphate,[12] and a "luxury" adsorption of phosphate by the plant. The total phosphate in soil No. 53 is very low and the total phosphate in No. 30 is subaverage. The total phosphate in both soils should decline rapidly because of luxury consumption by the plant and cause an absolute deficiency in a very few years.

Soils 1C and 75 give sufficient acid-soluble phosphate to account for a reasonably good supplying power in spite of substantial buffering. Since the soils are buffered, the adsorption complex could play little part in

[12] Soil No. 30 had originally the highest phosphate concentration of displaced solution of all encountered in this laboratory.

lowering the acid-soluble phosphate actually accessible to the plant even if the adsorption deficits were much higher than they are in both cases.

The physiological efficiency of soil No. 68A is unknown, but the comparatively high acid-soluble figures and low buffering capacity with the negligible adsorption capacity (adsorption index 0.14) indicates that the soil cannot be physiologically deficient at the present time.

We refrain from further analysis of these data because we realize that the limited number of soils and the incompleteness of our data with respect to the physiological supplying power of the soils could lead to erroneous conclusions as to the significance of specific figures obtained in the laboratory. We hope to present further evidence at a later date from larger numbers of soils, the physiological response of which is determined with three types of plants—plants with great acquisitive power for adsorbed phosphate, plants with slight acquisitive power, and plants with what may be called "average acquisitive power."

CONCLUSIONS

The phosphate-carrying particles of natural soils may be divided into two sharply defined classes—those which dissolve in acids (that is, both ions enter solution) and those which do not dissolve in acid, but which either hydrolyze in alkaline solutions or release phosphate only as a result of anion exchange. The phosphate accessible to plants (derived from acid-soluble particles) depends upon the PO_4-ion concentration of the soil solution[13] to a minor degree, and upon the amounts of PO_4 brought into solution by H ion at the interphase boundary between the root hair and the individual phosphate-carrying particle. The phosphate accessible to plants (derived from hydrolysis or from adsorbed phosphate) depends upon the degree of saturation of the hydrogels or adsorbing clay minerals and the amount of phosphate so held.

The phosphate brought into solution from the individual soil particles by acid cannot be exactly determined, but can be inferred from acid extractions, supplemented by a knowledge of the buffer capacity of the soil.

The amounts of phosphate on the hydrogels and clay minerals can be determined by extracting the soil with alkali. The degree of saturation of particles holding phosphate in this manner can be determined by comparing amounts of PO_4 extracted by alkali from the soil before and after saturation with phosphate.

We believe it possible to obtain limiting figures from chemical data, easily obtainable in the laboratory, which will indicate degrees of physio-

[13] As defined in this laboratory, that is, ions free to move in the water of the soil independently of solid phase or colloidal particles.

logical deficiencies in soils. We suggest certain preliminary and tentative figures and magnitudes, subject to change as a result of further studies of a larger group of soils and for plants of different sensitivities: If acid-extractable phosphate is high[14] (9 mg or more per 100 grams of soil), most plants will have no present difficulty in obtaining phosphate from the soil. If acid-extractable phosphate is low (about 1.0 mg or less), plants will usually acquire phosphate with difficulty, but the difficulty will be greatly enhanced if the buffer capacity is low and the adsorptive index is high. If the acid-extractable phosphate is intermediate, plants will probably have difficulty in acquiring phosphate when the buffer capacity is extremely high (compare soil 37 and soil 1C); or even in the absence of extreme buffering capacity, when the adsorption index is high.

The effect of a high adsorptive power (high adsorption index) in preventing a plant from acquiring potentially acid-soluble phosphate in the field is directly associated with the buffering power of the soil: (*a*) if the adsorption index is high and the buffering capacity is low, the conditions are highly adverse; (*b*) if the buffer capacity is high, the adsorption index is of no import in this connection.

The ability of a soil having a high adsorption index to deliver PO_4 from the adsorption complex to the plant in the field may be substantial for certain plants, provided that the degree of saturation and the number of particles carrying adsorbed phosphate is great, and if such plants can give off anions (for example, citrate) capable of being adsorbed. That plants with superior acquisitive power for phosphate have this power for the reason indicated is highly probable, particularly if the amount of contacts (root hair to soil particle) are great as a result of an extensive root development on the part of the plants.

Until further studies by the methods outlined have been performed with soils of very high organic-matter content, and on soils whose buffering capacity (or alkalinity) is due to sodium instead of calcium, we prefer to exclude such soils from our interpretation. We have data in hand which indicate that certain of our methods are applicable to peat soils, but the interpretations we have ventured above may have to be modified in some respects for this type of soil material.

SUMMARY

The causes of failure to obtain correlations between plant growth and the acid-extractable phosphate of soils are partly inherent and partly technical.

The rôles of adsorption complexes, hydrogels, and acid buffers, as

[14] By our technique.

affecting the analytical figures obtained by acid extraction of soils, are outlined.

The specific "acidity effect" of reagents cannot be measured in soils containing substantial amounts of adsorbing colloids if the anion of the reagent is itself adsorbed by the soil.

The kinds of chemical determination necessary in the prognosis of phosphate deficiency are announced.

A critical analysis of the quantitive effects of Ca ion and kaolinite in determining the phosphate solubility of a type soil is presented.

Hydrogen-ion concentration, phosphate concentration, present degree of saturation, and adsorption capacity of the adsorbing complex determine the removal of acid-dissolved phosphate both *in vitro* and in the field.

Chemical data on fourteen soils are analyzed in the light of these findings to illustrate how the present physiological supplying power of the soil could be deduced from the data.

Tentative standards represented by figures and magnitudes are suggested as a basis for predicting the current phosphate-supplying power of soils.

ACKNOWLEDGMENT

We are especially indebted to P. L. Hibbard of this laboratory, whose extensive studies of the acid solubility of soil phosphate have indicated the desirability of using dilute acid and the importance of interpreting results of acid extraction with reference to the buffering capacity of soils.

LITERATURE CITED

1. BURD, JOHN S., and J. C. MARTIN.
   1923. Water displacement of soils and the soil solution. Jour. Agr. Sci. 13(pt. 3): 265–95.
2. COMBER, NORMAN M.
   1924. The rôle of the electronegative ions in the reactions between soils and electrolytes. p. 567–72. *In:* Base exchange in soils. Faraday Soc. Trans. **20**:551–617. (Published also as a separate.)
3. FISHER, E. A.
   1921. The phenomena of absorption in soils: a critical discussion of the hypotheses put forward. p. 305–16. *In:* Physico-chemical problems relating to the soil. Faraday Soc. Trans. **17**(pt. 2):217–368. (Published also as a separate.)
4. HIBBARD, P. L.
   1930. Chemical methods for estimating the availability of soil phosphate. Soil Sci. 31(6): 437–66.
5. MURPHY, H. F.
   1938. The rôle of kaolinite in phosphate fixation. Hilgardia **12**(5):342–82.
6. RUSSELL, E. JOHN.
   1937. Soil conditions and plant growth. 7th ed. 655 p. Longmans, Green & Co., London.
7. RUSSELL, E. J., and J. A. PRESCOTT.
   1916. The reaction between dilute acids and the phosphorus compounds of the soil. Jour. Agr. Sci. **8**(pt. 1):65–110.
8. TEAKLE, L. J. H.
   1927. Phosphate in the soil solution as affected by reaction and cation concentrations. Soil Sci. **25**(2):143–62.
9. TIULIN, A. F.
   1935. Critical zones of absorbed ions and their availability for plant life. Internatl. Soc. Soil Sci. Soviet Section Trans. Vol. **A**:70–78.

THE RÔLE OF KAOLINITE IN PHOSPHATE FIXATION

H. F. MURPHY

CONTENTS

PAGE

Phosphate-fixation systems 343
Group 1, chemical precipitation 343
Group 2, mutual precipitation of phosphates by iron, aluminum, and silica hydrogels 344
Group 3, adsorption of phosphates by alumino-silicates 345
General experimental methods 346
Influence of iron on phosphate fixation 346
Iron hydrosols at different pH values in the presence of an excess of hydrosol 346
Iron phosphates at different pH values in the presence of an excess of iron 348
Discussion of experiments with iron 349
Studies on a soil having a high fixing power 350
Composition 350
The release of phosphate by acid treatment 350
The recovery of phosphate from superphosphate treatments with dilute NaOH 351
The recovery of phosphate from superphosphate treatments by acid equilibrium systems 351
The recovery of phosphate from superphosphate treatments by acid leaching 353
Phosphate-fixation capacity 353
The effect of grinding 354
Discussion of Aiken-clay loam investigations 354
Investigations with kaolinite 356
Retention of phosphate by crushed kaolinite 356
The effect of grinding 356
The effect of reaction as indicated by leaching 357
The effect of reaction as indicated by equilibrium study with PO_4 constant 358
The effect of reaction as indicated by equilibrium study with both K and PO_4 constant 358
The effect of concentration on phosphate fixation 358
The effect of heating 358
The effect of time 361
The effect of degree of saturation with respect to PO_4 on cation exchange capacity 361
The effect of the oxalate ion on the adsorption of phosphate by kaolinite 362
Discussion of kaolinite investigations 363
Comparison of kaolinite with other clay materials 366
Greenhouse tests of phosphate fertilizer on Aiken clay loam 367
The effect of rate and placement 367
The effect of soil reaction 368
The effect of source of nitrogen 369
The effect of a good starting medium 371
The effect of size of superphosphate particles 372
Greenhouse tests of comparative value of superphosphate and "kaolinite phosphates" 372
Greenhouse tests of the effect of various colloids on superphosphate efficiency 373
Discussion of results 374
Summary 377
Acknowledgments 378
Literature cited 379

THE RÔLE OF KAOLINITE IN PHOSPHATE FIXATION[1, 2]

H. F. MURPHY[3]

WHEN A SOLUBLE PHOSPHATE is brought in contact with the soil, reactions take place which remove a great deal, if not all, of the phosphate from solution. This phenomenon has been called "the fixation of phosphates by soils." Such a term carries no implication of the means by which removal takes place or of the product formed; it conveys only the idea that the phosphate has been changed and is present in some form that is only slightly soluble under the prevailing conditions. To the scientist who is interested in soil relations, plant relations, and the complex soil-plant system, more than the mere fact that the "phosphate is fixed by the soil" is required. The mechanism of the fixation is important to the soil specialist, while the means of resupplying the soil solution or the plant from the phosphate so held is important to the plant physiologist.

The investigations reported here were undertaken to obtain more fundamental data on the manner of phosphate fixation in soils not controlled by the calcium system.

PHOSPHATE-FIXATION SYSTEMS

The reactions converting phosphates into less soluble forms are several in number. The various types of fixation may now be classified into a few groups, which will be discussed in the following paragraphs.

Group 1, Chemical Precipitation.—Until rather recently, chemical precipitation has been considered the primary cause of phosphate fixation in all soils. This precipitation has been attributed largely to Ca, Fe, Al, Mg, and Mn.

A great many soils are governed by what may be termed the "calcium system." Soils with such a system predominate in arid and semiarid regions and also occur in the more humid sections. In these soils, calcium is the predominating cation, although leaching may have removed it to a considerable degree. In some instances, leaching has been so severe that the only calcium left is found in a few local zones, and the soils are very acid. Such soils cannot be considered strictly within this group and will

[1] Received for publication June 22, 1938.

[2] Submitted in partial fulfillment of the requirement for the Degree of Doctor of Philosophy in the University of California.

[3] Graduate student of the University of California 1930–31, and 1937–38; now Associate Professor of Soils, Oklahoma Agricultural and Mechanical College.

not be dealt with here. Where calcium is the controlling cation, it reacts with soluble phosphates and withdraws the phosphate ions from solution. Calcium phosphates, however, are appreciably soluble in an acid medium; therefore, the production or introduction of a hydrogen-ion producing substance tends to redissolve the calcium phosphates formed.

Teakle (*46*)[4] has shown that calcium phosphates are relatively insoluble on the alkaline side of neutrality, and in the presence of an excess of calcium, they become insoluble at about pH 6. This means that to liberate phosphate for plant use in such a system hydrogen ions must be produced in an amount sufficient to lower the pH at the absorbing surface below this value. Slightly acid soils belonging to this system and having an appreciable amount of calcium in the replaceable form are able to supply the plant with phosphate without difficulty, provided the potential supply is adequate. Gaarder and Nielsen (*15*) have shown the behavior of the phosphate ion in the presence of free ions of iron, aluminum, calcium, sodium, and magnesium.

In acid soils, the fixation of phosphates has been considered as due to the precipitation of $FePO_4$ and $AlPO_4$. The probability is against such a simple fixation, because free Fe and Al ions are not present in the soil solution to any appreciable extent except in very acid soils. That $FePO_4$ and $AlPO_4$ may be partially precipitated from an artificial system at pH ranges common to acid soils is ably shown by several investigators (*46, 9*), but this does not prove that Fe or Al ions are present in sufficient quantity to fix applied soluble phosphates rapidly. Moreover, certain experiments (*32*) have indicated the accessibility of such phosphates to plants at pH values of 6 and 7. If $FePO_4$ and $AlPO_4$ were the products of fixation, it would seem that soils having a fair supply of phosphate and within this range of soil reaction should be able to supply the plant with the necessary phosphorus for growth. Truog (*48*) found that precipitated $FePO_4$ and $AlPO_4$ produced, with a few exceptions, good growth.

Group 2, Mutual Precipitation of Phosphates by Iron, Aluminum, and Silica Hydrogels.—Evidences of the adsorption type of reaction have accumulated during the last few years. Russell and Prescott (*42*) in 1916 ascribed some of their results to adsorption phenomena, but the criticism of their work by Fisher (*11*) and by Comber (*5*) discredited the idea for a time. In 1921 Harrison and Das (*20*) concluded that in noncalcareous soils the retention of P_2O_5 is mainly due to adsorption, whereas in calcareous soils retention by adsorption is either nonexistent or entirely masked by other causes. Shortly thereafter, the work of Gordon and his

[4] Italic numbers in parentheses refer to "Literature Cited" at the end of this paper.

associates (*19, 25, 45*) and of Mattson (*27–30*) began to appear in the literature in support of a colloidal mechanism. Other recent investigations (*6, 18, 31, 33, 34, 35, 37, 38*) furnish confirming evidence of this kind of action.

The simpler iron and aluminum compounds found in the soil are oxides or hydrous oxides. While iron and aluminum ions may be present, the amount of these is appreciable only when the soil becomes very acid. The ordinary soil solution is very low in these ions as well as in phosphate ions. These facts lend support to the idea that the hydrated oxides of these materials, because of their colloidal nature, are responsible for considerable adsorption of phosphate ions. Heck (*21*) considers the active iron and aluminum in soils as existing in the forms of hydrated oxides.

Artificially prepared hydrogels and hydrosols of iron and aluminum have been shown (*16, 25, 45, 47*) to remove PO_4 from solution. Gordon and his associates (*25, 51*) found that while iron and aluminum hydrogels were able to hold on to the adsorbed phosphate tenaciously against distilled water and certain sulfates, 0.1*N* solutions of NaOH and NH_4OH were capable of removing some of the adsorbed phosphate, and the plants were able to utilize PO_4 from the freshly prepared material. Ellett and Hill (*10*) stated in 1917 that "if the yield is taken as a measure of availability, iron and aluminum do not fix phosphoric acid in forms unavailable to the wheat plant." In their experiments, they used iron and aluminum hydroxides as fixing agents for monocalcium phosphate and superphosphate (acid phosphate). Tiulin (*47*) prepared an iron gel of varying degrees of saturation of phosphate and showed that plants were able to secure phosphorus from it in accordance with the degree of saturation. Ford (*12, 13*) and Dean (*7*) present evidence showing the formation of complex phosphate addition compounds to certain hydrated iron and aluminum oxides. Mattson (*29*) and Pugh (*35*) have demonstrated that the phosphate content of the iron or aluminum hydrogel complex is variable; it increases as pH is lowered and decreases as the pH is raised.

Group 3, Adsorption of Phosphates by Alumino-Silicates.—Mattson (*30*) shows that artificially prepared alumino-silicates as well as some naturally occurring colloids containing silica are capable of adsorbing phosphates, and that the PO_4 content of the complex varies indirectly with pH. Pugh and du Toit (*36*) report that silicates and phosphates may be regarded as substituted hydroxides, and that the OH ion replaces SiO_3 and PO_4 ions in exactly equivalent proportions in synthesized ferric silicates and phosphates.

Roszmann (*40*) suggests the possibility that the clay complex fixes

phosphate. Bradfield (*2*) suggests that phosphates may in part be retained on the surfaces of the colloidal alumino-silicates in the soil, and that other anions may replace it. Scarseth (*44*) found that a prepared bentonite retained phosphate, and suggested that the adsorption on the colloidal surfaces at pH 5.5 to 6.1 was due to the aluminum valence. "Ferriferated" bentonite increased the phosphate retained. The PO_4 ion was found to be replaceable by OH and SiO_4 anions.

Gilbert (*17*) reported that normal phosphate fertilization of some Rhode Island soils during a period of thirty-five years had not reduced the power of phosphate adsorption significantly, irrespective of the phosphate carrier used. A high rate of liming reduced the adsorption power. Furthermore, phosphate was fixed by these soils from buffer solutions of monopotassium phosphate adjusted to pH 5, 6, and 7; but was given up by the soil when the pH was lowered to 2 or was raised above 10. Truog (*48*) showed that freshly precipitated iron and aluminum phosphates were utilizable by plants; but that after the first crops they were less so, and suggested that these older basic phosphates may have combined with acid silicates to form very resistant insoluble compounds.

GENERAL EXPERIMENTAL METHODS

The methods employed were varied according to the nature of the individual experiments and are described briefly in connection with these experiments. A few methods were common to many experiments, however, and these are described at this point to avoid repetition. The phosphates were determined volumetrically by the usual ammonium molybdate procedure. Potassium was determined volumetrically by titrating the precipitated potassium cobalti-nitrite with standard $KMnO_4$. The pH values were determined by the glass electrode except in the greenhouse experiments, where the hydrogen electrode was employed. Where shaking was employed, it was generally done on rollers which turned the containers slowly along their horizontal axes. Exceptions to this shaking procedure will be noted.

INFLUENCE OF IRON ON PHOSPHATE FIXATION

Iron Hydrosols at Different pH Values in the Presence of an Excess of Hydrosol.—In experiment 1a, a solution of $FeCl_3$ was made of such concentration that when the other reagents were added, 500 cc contained 340 mg of Fe. The iron was precipitated as hydroxide at various pH values by the use of different amounts of dilute NH_4OH. A solution of KH_2PO_4 sufficient to furnish 175.6 mg of PO_4 was then added to make a total volume of 500 cc in each case. The suspensions were shaken by

hand, and after standing for about 1 day, the filtrates were tested for PO_4. The results are given in table 1.

TABLE 1

THE RETENTION OF PHOSPHATE IN THE PRESENCE OF AN EXCESS OF IRON HYDROSOL

Color of filtrate	Reaction		PO_4 fixed	
	Suspension	Filtrate	Amount	Per cent*
	pH	*pH*	*mg*	*per cent*
Reddish amber	2.13	2.14	15.60	8.88
Clear amber	2.23	2.26	85.60	48.74
Very slightly yellow	2.53	2.64	173.35	98.72
Water-clear	2.82	3.11	173.85	98.98
Water-clear	4.94	5.09	170.35	97.01
Water-clear	6.50	6.50	129.60	73.80
Water-clear	7.36	7.32	110.60	62.98
Water-clear	8.12	8.17	94.60	54.44

* PO_4 fixed as a percentage of that added.

The amount of iron (340 mg) was arbitrarily chosen, but represents the amount removed from 100 grams of Aiken clay loam in citric acid (1:5) equilibrium extract.[5] The exact procedure was to digest 10 grams of soil with 100 cc of *N* citric acid on a steam bath for ½ hour. The PO_4 used was approximately equal to the total PO_4 content of 100 grams of this soil.

TABLE 2

THE INFLUENCE OF pH ON $FePO_4$ PRECIPITATION IN THE PRESENCE OF AN EXCESS OF IRON

Color of liquid	Reaction		PO_4 fixed	
	Suspension	Filtrate	Amount	Per cent*
	pH	*pH*	*mg*	*per cent*
Amber	2.10	2.10	105.00	60.00
Amber	2.27	2.27	150.60	85.76
Slight amber	2.51	2.56	165.60	94.30
Slight yellow tinge	2.79	2.92	170.35	97.01
Water-clear	3.17	3.47	174.35	99.29
Water-clear	5.87	6.12	171.85	97.86
Water-clear	7.33	7.80	175.35	99.86
Water-clear	7.80	7.82	174.56	99.41
Water-clear	8.24	8.27	173.10	98.57

* PO_4 fixed as a percentage of that added.

In experiments 1a and 1b, the hydrosol was formed before adding the phosphate solution, whereas in experiments 2a and 2b the phosphate solution was added to the iron solution before adding the NH_4OH. This

[5] Hagan, R. M. Physiological deficiency in soils as related to mechanism of phosphate release. Unpublished manuscript. 1937.

has a considerable bearing on the retention of PO_4, as will be recognized in comparing the graphs in figures 1 and 2. Figure 1, curve *a*, is a graphic representation of the data in table 1.

In experiment 1b, the same procedure as in experiment 1a was used except that the amount of $FeCl_3$ was only in slight excess of that neces-

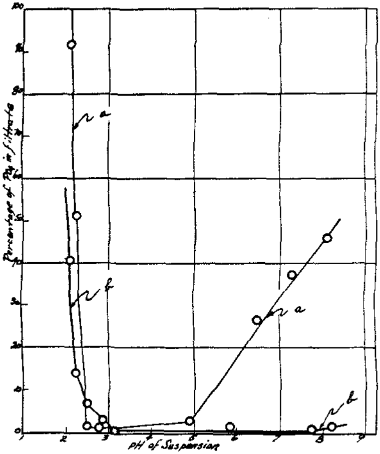

Fig. 1.—Curve *a*, the influence of pH on the adsorption of phosphate by an iron hydrosol containing a large excess of Fe over PO_4; curve *b*, the influence of pH on the precipitation of phosphate in the presence of a large excess of Fe.

sary to combine with PO_4 to give $FePO_4$. The results are graphically represented in figure 2, curve *a*.

Iron Phosphates at Different pH Values in the Presence of an Excess of Iron.—In experiment 2a, a solution of $FeCl_3$ was added to a KH_2PO_4 solution, and the pH was changed by adding various amounts of dilute NH_4OH. The total volume was 500 cc and contained 340 mg of Fe and 175.6 mg of PO_4. The shaking and period of standing were the same as in experiment 1a. The results are recorded in table 2 and are shown graphically in figure 1, curve *b*.

In experiment 2b, the same procedure as in experiment 2a was used except that the amount of $FeCl_3$ employed was in only slight excess of

that necessary to combine with the PO_4 to give $FePO_4$. The results are shown graphically in figure 2, curve *b*.

Discussion of Experiments with Iron.—The data indicate that even in the presence of an excess of iron hydrosol an appreciable amount of PO_4 is left in solution at pH values of 6 and above. Hence, if hydrous iron

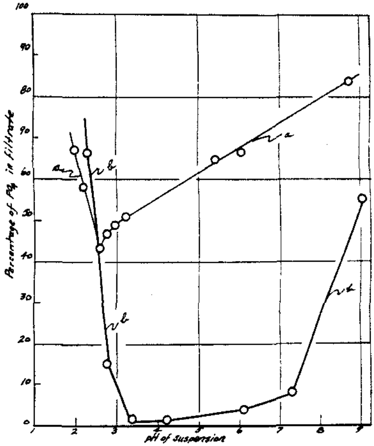

Fig. 2.—Curve *a*, the influence of pH on the adsorption of phosphate by an iron hydrosol containing only a slight excess of Fe over PO_4; curve *b*, the influence of pH on the precipitation of phosphate in the presence of a slight excess of Fe.

oxides are functioning as the adsorbing system in a given soil, at pH values of about 6 there should be considerable PO_4 in the soil solution available for plants, especially after applying a fertilizer containing soluble phosphate.

Not much iron is found in the soil solution until a high acidity is reached; therefore, the fixation as $FePO_4$ (the *b* curves in figs. 1 and 2) has a very limited effective range and could not account for rapid fixation in soils having only a slight acidity. Fixation by iron in such a pH range would be largely limited to the hydrous oxides present. Free nonhydrated iron oxide (hematite) has been found (*13*) unable to fix phosphate.

STUDIES ON A SOIL HAVING A HIGH FIXING POWER

Certain soils have greater capacity to remove phosphates from solution than others. Colloids from such soils are characterized by having a low silica : sesquioxide ratio. The Aiken soil series is representative of this group and has been chosen for the studies involved.

Composition.—The composition of Aiken clay loam and its colloid was determined by the methods of the Association of Official Agricultural Chemists (*1*). The colloid was secured by placing 1 kg of soil in a 5-gallon earthenware jar, agitating thoroughly each day, and removing the top 8 cm of suspension every 24 hours. This was carried out over a 30-day period. The suspension was filtered with Pasteur-Chamberlain filter tubes using suction. The chemical analyses of soil and colloid are given below:

Constituent	Soil, per cent	Colloid, per cent
SiO_2	38.63	30.98
Fe_2O_3	12.42	12.40
Al_2O_3	34.43	39.90
CaO	1.68	1.68
MgO	1.20	1.05
PO_4	0.18	0.22
Ignition loss	15.41	17.40

The ratios were as follows:

$SiO_2 : Al_2O_3$	1.90 : 1	1.32 : 1
$Fe_2O_3 : Al_2O_3$	0.23 : 1	0.20 : 1
$SiO_2 : R_2O_3$	1.54 : 1	1.10 : 1

The percentage phosphate content of the colloid is higher than that of the soil. This is in accordance with data of other investigators (*3, 12*) who have made a study of the distribution of the chemical constituents in the various soil separates. It indicates that the finer fractions of the soil have a higher capacity for combining with soluble phosphates.

The Release of Phosphate by Acid Treatment.—Tests were made with HCl at various strengths on untreated Aiken clay loam. The ratio of soil to solution in each case was 1 : 5.

Such tests, if the acidity is great enough to dissolve appreciable quantities of iron and aluminum, should liberate increasing amounts of PO_4 if the PO_4 already present in the soil is in the form of iron or aluminum phosphate. Particularly is this the case if the pH is below 2.5, as is shown by figures 1 and 2. The results (table 3) did not indicate any increase in the PO_4 content of the filtrate with increase in HCl from equilibrium mixtures shaken for 1 hour. Evidently such minerals are absent; or if

present, their presence is obscured by a secondary reaction involving clay minerals of a type discussed in a later section.

The Recovery of Phosphate from Superphosphate Treatments with Dilute NaOH.—Four percolators were filled with air-dried Aiken clay loam. The cross-sectional soil area at the top of the percolator was equivalent to 1/500,000 acre. The soil was moistened to field capacity with distilled water, and superphosphate of various-sized particles was placed

TABLE 3

PO_4 LIBERATED FROM AIKEN CLAY LOAM BY DIFFERENT HCl SOLUTIONS

Approximate normality of acid	Reaction of suspension	Fe in solution*	PO_4 in filtrate per 100 grams of soil
N	*pH*		*mg*
0.100	1.66	+++	<0.2
0.075	1.68	+++	<0.2
0.050	2.16	++	<0.2
0.025	2.93	++	<0.2
0.010	4.16	Trace	<0.2
0.002	5.64	None	<0.2
0.001	5.83	None	<0.2

* As shown by NH_4OH precipitation.

on top of the moistened soil surface of each percolator at the rate of 600 pounds per acre. The soils were leached with distilled water until 2,000 cc of leachate was secured from each percolator. This required approximately 2 days. The samples were allowed to stand in the percolators and air-dry for one week. They were then divided into layers. A 1:5 suspension of each of the various soil layers in 0.1*N* NaOH was made. The samples were shaken 1 hour, filtered, and the PO_4 content of the filtrate was determined.

Sodium hydroxide was chosen as a medium because numerous experiments (*50* and unpublished data[6]) have shown that low figures are secured from its use if the PO_4 in the soil is controlled by a calcium equilibrium system; furthermore, high figures are secured where the phosphate is in the form of iron or aluminum phosphate or is held by adsorption. Hydrolysis of iron and aluminum phosphates occurs as the pH is increased above pH 7 (*15, 26, 46*).

The results are reported in table 4.

The Recovery of Phosphate from Superphosphate Treatments by Acid Equilibrium Systems.—Previous experiments,[7] as well as those performed by the writer (table 3), show that ordinary acid equilibrium

[6] Burd, J. S., unpublished data.

[7] Hagan, R. M. Physiological deficiency in soils as related to mechanism of phosphate release. Unpublished manuscript. 1937.

extractions of this soil give practically no PO_4 in the filtrate. However, according to table 4, more of the added phosphate remained in the soil as a calcium phosphate when larger rather than when small particles of superphosphate were used; these results indicate that perhaps an acid extraction would give a further indication of this amount.

TABLE 4

THE INFLUENCE OF PARTICLE SIZE ON THE RECOVERY OF PO_4 FROM SUPERPHOSPHATE BY 0.1*N* NaOH

Treatment	Depth	Weight of soil fraction	Total PO_4 soluble in 0.1*N* NaOH	PO_4 not recovered*
	inches	*grams*	*mg*	*mg*
10- to 20-mesh† superphosphate; 156.8 mg PO_4	0.0–0.5	109.7	99.15	
	0.5–1.0	117.9	41.18	
	1.0–2.0	130.1	38.12	
	2.0–3.0	96.0	19.20	
	3.0–4.0	88.0	22.88	
	4.0–5.0	91.0	19.11	
	Total	632.7	239.64	56.99
Untreated‡	.....	632.7	139.83	
60- to 100-mesh superphosphate; 167.2 mg PO_4	0.0–0.5	115.5	103.56	
	0.5–1.0	111.9	42.03	
	1.0–2.0	144.8	48.88	
	2.0–3.0	101.0	20.20	
	3.0–4.0	73.0	17.52	
	4.0–5.0	99.0	22.77	
	Total	645.2	254.96	54.83
Untreated‡	....	645 2	142 59	
Finer than 200-mesh superphosphate; 153.3 mg PO_4	0.0–0.5	81.4	81.33	
	0.5–1.0	107.8	40.92	
	1.0–2.0	148.4	63.54	
	2.0–3.0	103.0	28.84	
	3.0–4.0	102.0	24.48	
	4.0–5.0	95.0	27.55	
	Total	637.6	266.66	27.55
Untreated‡	....	637.6	140.91	

* This is calculated from the amount of PO_4 added in the superphosphate, the amount of PO_4 0.1*N* NaOH extracted from untreated soil, and the amount of PO_4 the NaOH actually extracted from the treated soil.

† This means that the superphosphate passed through a 10-mesh sieve, but was retained on a 20-mesh sieve.

‡ 0.1*N* NaOH removed 22.10 mg of PO_4 from 100 grams of untreated soil.

Accordingly, the equivalent of 20 grams of moisture-free soil from the 0.0–0.5-inch layer of each treatment was shaken for 1 hour with HCl so as to furnish a 1:5 filtrate with a pH of 3. The results are shown in table 5.

The experiment is inconclusive, since the acid may have dissolved the residual calcium phosphate; and this may have been immediately adsorbed by the soil colloids.

The Recovery of Phosphate from Superphosphate Treatments by Acid Leaching.—The purpose of acid leaching was to determine if, during the HCl equilibrium experiment, any phosphate was dissolved which was subsequently fixed.

Three 100-gram samples of Aiken clay loam were weighed out, one was

TABLE 5

HCl EQUILIBRIUM AND HCl LEACHING STUDIES OF AIKEN CLAY LOAM AFTER TREATING WITH SUPERPHOSPHATE

Fineness of superphosphate used	HCl equilibrium studies*: Reaction of suspension	HCl equilibrium studies*: PO_4 in filtrate per 100 grams of soil	HCl leaching—PO_4 in filtrate per 100 grams of soil†
	pH	*mg*	*mg*
10- to 20-mesh	3.07	0.2	29.77
60- to 100-mesh	3.07	0.2	....
Finer than 200 mesh	2.99	0.2	15.04
None	2.93	0.2	Trace

* 20 grams of soil from 0.0–0.5-inch layer of treatment in table 4 used in this experiment.

† 560 mg of superphosphate per 100 grams of soil used.

treated with 560 mg of 10- to 20-mesh superphosphate, one was treated with 560 mg of superphosphate finer than 200-mesh, and no phosphate was added to the third.

The superphosphate was thoroughly mixed with the soil. The samples were placed in pint jars and 50 cc of distilled water were added. The jars were loosely closed to prevent evaporation and were kept at room temperature for 8 days. At the end of this time, the soil was removed from each jar and spread out in a thin layer over 15-cm filter papers in Buechner funnels. Each sample was leached rapidly with 500 cc of 0.1*N* HCl, filtering being hastened by suction. The time required was 5 minutes. Samples of the filtrates were tested for their phosphate content. The results are tabulated in table 5.

Phosphate-Fixation Capacity.—Samples of 100 grams of Aiken clay loam were shaken for 1 hour with 500 cc of water and enough monocalcium phosphate to furnish the amounts of PO_4 shown in table 6. The samples were filtered, and the PO_4 content of the filtrates was determined.

The residues were re-treated with the same quantities of monocalcium phosphate as in the first treatment, and the rest of the procedure repeated. In table 6 are also recorded the amounts of PO_4 fixed by this second treatment, and the combined fixation for both treatments.

The Effect of Grinding.—A 75-gram charge of the Aiken clay loam was ground in a ball mill for 6 days. Its ability to fix phosphate was determined along with that of unground soil, Aiken colloid, and kaolinite that had been ball-milled for 9 days.

The procedure followed was to weigh out 1-gram samples into small bottles; add 50 cc of KH_2PO_4 solution (pH 4.48) containing a total of 355.24 mg of PO_4, and shake for 100 hours. After the shaking process, the suspensions were allowed to stand for 1 day to permit the settling out of the solid materials. The PO_4 content of the filtrates was then determined. The results were as follows:

Substance	pH of filtrate	PO_4 fixed per 100 grams of soil, mg
Aiken clay loam	5.22	2,372
Aiken clay loam, ball-milled	5.89	6,232
Aiken colloid	5.51	3,858
Kaolinite, ball-milled, 9 days	6.07	10,988

Discussion of Aiken-Clay-Loam Investigations.—The analyses (p. 350) indicate that the soil chosen for the study has a low silica : sesquioxide ratio, and that the total iron content is much the same in the colloidal and noncolloidal fractions.

If all the iron in the soil were active and free to combine with PO_4, 100 grams of the soil would be able to fix approximately 14.7 grams of PO_4. If only the iron in the clay fraction is active (calculation would indicate approximately 50 per cent of the soil is colloidal matter) the 100 grams of soil would be able to fix about 7.3 grams of PO_4.

The 100 grams of soil (table 6), after two exposures to a high concentration of monocalcium phosphate, retained approximately 2.5 grams of PO_4. This would require that between 25 and 30 per cent of the iron in the clay fraction be active and free to combine. If the soil had been treated with more phosphate, more PO_4, would probably have been fixed.

Unpublished data[8] indicate that normal citric acid removes approximately one-third of a gram of iron from 100 grams of this soil. Assuming that this is all the iron that is free to react with PO_4, it could combine with only about 0.6 grams of PO_4. The soil actually retained more than four times this amount (table 6). The pH of normal citric acid is 1.82, which is much below pH 4.26, the pH of the filtrate after fixation from the high concentration of monocalcium phosphate; and that much acidity should bring into solution, if not all, at least most, of the iron which is free to react with the phosphate to form $FePO_4$ or the iron phosphate complexes.

[8] Hagan, R. M. Physiological deficiency in soils as related to mechanism of phosphate release. Unpublished manuscript. 1937.

The active iron that could be instrumental in the fixation process must be of a hydrous oxide form and have sufficient surface exposure. In view of the amount dissolved by citric acid, iron of this character could scarcely be present in sufficient amount.

After the soil is ground in the ball mill, its ability to fix phosphate increases very greatly, which would indicate other factors are entering into the problem of phosphate fixation in this soil.

The fixation capacity is extremely high, and therefore saturating the soil with phosphate would apparently be impractical. When a heavy application is made, however, some phosphate is left for plant use.

TABLE 6

PHOSPHATE FIXATION BY AIKEN CLAY LOAM WITH TWO MONOCALCIUM PHOSPHATE TREATMENTS

Sample No.	PO_4 added (each treatment)	PO_4 in filtrate	PO_4 fixed per 100 grams of soil					
			First treatment		Second treatment		Total	
	mg	*mg*	*mg*	*per cent*	*mg*	*per cent*	*mg*	*per cent*
1..........	25.26	0.35	24.29	96.16	23.61	93.47	47.90	94.81
2..........	125.91	2.55	123.36	97.97	109.00	86.57	232.36	92.27
3..........	624.85	152.61	472.24	75.58	275.41	44.08	747.65	59.83
4..........	3,125.76	1,693.93	1,431.83	45.81	1,036.65	33.16	2,468.48	39.49

The low figures secured with the acid treatments on the fertilized soil (table 5) indicate a high degree of fixation and precludes the presence of much calcium phosphate. These data, however, do not tell where the fixation took place in the soil column.

Since NaOH extracts give large figures for iron, aluminum, and colloidally formed phosphates, they can be used to determine in which soil layers the fixation occurred. The data in table 4 show that extreme fixation took place in the surface ½ inch of soil and in no case was there any appreciable penetration of the applied phosphate below a depth of 2 inches.

The larger particles of fertilizer appear to have some advantage over the finer particles in retaining their phosphate as calcium phosphate in the soil. This is indicated by the acid-leaching data given in table 6. Because of the limited leaching, these figures cannot be taken as the total amount of calcium phosphate present, but they represent a high percentage of it.

A concentrated HCl digestion of the coarse particles which were removed from the acid-leached soil showed that they contained a total of 21 mg of PO_4. Hence, the coarse particles after a week's contact with moist soil retained less than one-third of their original phosphate content.

INVESTIGATIONS WITH KAOLINITE

The failure to secure an increase in released PO_4 (table 3, p. 351) when the soil was extracted with HCl at pH 2 and lower (the reaction at which phosphated iron hydrosol and iron phosphate are both soluble) lead to an investigation of the type of clay present in the soil, and its capacity to remove phosphate from solutions. X-ray investigations showed that the

TABLE 7
THE RETENTION OF PHOSPHATE BY CRUSHED KAOLINITE
(Suspension* shaken 1 hour)

Test No.	Weight of kaolinite	PO_4 added	PO_4 fixed per 100 grams of kaolinite
	grams	*mg*	*mg*
1	25	23.33	25.0
2	20	17.57	23.7
3*	20	8.79	22.5
Average	..	.....	23.7

* 1.0:5.0 suspension for tests 1 and 2, 1.0:2.5 suspension for test 3.

clay was kaolinic in character (fig. 3, *B*). Data presented on page 350 show it to have a low silica : sesquioxide ratio.

Retention of Phosphate by Crushed Kaolinite.—Since the clay was so identified, samples of crushed kaolinite were tested for their ability to fix phosphate from a 1 :5 suspension of dilute monocalcium phosphate. The shaking was for a 1-hour period.

The results are recorded in table 7.

The rather coarse kaolinite used fixed PO_4 at the rate of 23.7 mg per 100 grams. This establishes a rather high fixing power even for fairly coarse kaolinite, and immediately suggests a probable source of fixation for soils (containing kaolinite) whose fixing capacity cannot be assigned to precipitation by calcium or to mutual precipitation with iron or aluminum hydrosols.

The Effect of Grinding.—In an experiment to determine the effect of fineness of kaolinite upon the quantity of PO_4 fixed, a sample of 125 grams of kaolinite was placed in a ball mill for 6 days. At the end of this time all but 50 grams was removed. The 50-gram charge was left in the mill, and at intervals 1-gram samples were removed. The ability of the various samples ground for different periods of time to fix phosphate was determined. In making this determination, 1-gram samples were placed in small bottles with 50 cc of KH_2PO_4 solution containing 6.8 mg of PO_4 per cc and having a pH of 4.47. The suspensions were shaken on a roller

for 100 hours. They were removed and allowed to settle for 1 day, when the phosphate content of the supernatant liquid was determined.

The results are recorded in table 8. Grinding increased immensely the capacity of the kaolinite to retain phosphate. Since the kaolinite in the soil is in a finely divided condition, it must have a great capacity to fix phosphate.

The Effect of Reaction as Indicated by Leaching.—A solution of KH_2PO_4 was modified by the addition of NaOH and water so as to give

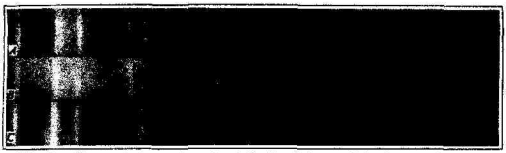

Fig. 3.—X-ray photographs: *A*, of the kaolinite used in the experiments; *B*, of the Aiken colloid; *C*, of a referee sample of kaolinite.

solutions having pH values of 4.54, 6.23, 6.43, and 7.90. Each of these solutions had the same K and PO_4 content (1.1 and 2.8 mg per cc, respectively), but the sodium content varied according to the amount of NaOH necessary to change the pH. Kaolinite, which had been ground in a ball mill for 5 days in a 150-gram charge and then 2 days in a 75-gram charge,

TABLE 8

THE EFFECT OF GRINDING KAOLINITE ON PHOSPHATE FIXATION
(1:50 suspension with KH_2PO_4 solution per 100 cc; shaken 100 hours)

Size of charge	Cumulative grinding time	pH of filtrate	PO_4 fixed per 100 grams of kaolinite
grams	*days*	*pH*	*mg*
....	Storeroom sample	4.59	822
125	6	5.43	4.752
50	7	5.63	6.332
49	8	5.69	8.114
48	12	5.72	9.104
47	15	5.78	10,292

was weighed out in four 10-gram lots, placed in beakers; and 100 cc of solution was added, a different solution being placed in each beaker. The beakers and their contents were warmed in a water bath at 70° C for 3 hours. The suspensions were filtered with suction. The residue was then washed with three additional portions (15 cc, 50 cc, and 25 cc) of the

same phosphate solution as had been used earlier. The PO_4 content of the solutions less that in the filtrates was considered as the phosphate fixed by the kaolinite. The results are given in table 9.

The Effect of Reaction as Indicated by Equilibrium Study with PO_4 Constant.—One-gram samples of kaolinite, which had been ground in a ball mill for 7 days in a 75-gram charge, were suspended in 50-cc portions of solutions of KH_2PO_4 with different pH values. This amount of phos-

TABLE 9

THE FIXATION OF PHOSPHATE AT VARIOUS REACTIONS BY KAOLINITE AND ITS INFLUENCE ON THE REACTION OF THE FILTRATE

Reaction		PO_4 fixed per 100 grams of kaolinite	K fixed per 100 grams of kaolinite
Original solution	Filtrate		
pH	*pH*	*mg*	*mg*
4.54	6.20	1,956.7	342.5
6.23	6.40	1,243.3	491.7 (?)
6.43	6.40	863.8	409.3
7.90	7.24	274.9	452.9

phate solution contained 98.55 mg of PO_4. The pH was adjusted by the addition of KOH. The suspensions were shaken for 6 hours, and after standing 1 day, the supernatant liquid was analyzed.

The results are summarized in table 10.

The Effect of Reaction as Indicated by Equilibrium Study with Both K and PO_4 Constant.—Solutions of H_3PO_4, KOH, and KCl were mixed and made to volume to give solutions with different pH values but with a constant PO_4 and K content: 50 cc contained 183.8 mg of K (except where otherwise noted) and 160.7 mg of PO_4. One-gram samples of kaolinite ground as in the preceding experiment were suspended in 50 cc of each solution. The suspensions were shaken for 20 hours, then centrifuged, and the supernatant liquid analyzed immediately. The results are given in table 11.

The Effect of Concentration on Phosphate Fixation.—The effect of the concentration of KH_2PO_4 on phosphate fixation was studied in connection with different amounts of kaolinite which had been ground in a ball mill for 7 days. The total volume of solution was 25 cc in all cases. The kaolinite was weighed out in series of 1.0-gram, 2.5-gram, and 5.0-gram samples and one sample of each weight was added to each KH_2PO_4 solution. The suspensions were shaken for 12 hours, allowed to stand 7 days, filtered, and the filtrates were analyzed. The results are given in table 12.

The Effect of Heating.—According to several investigators (*24, 39*), kaolinite breaks down when heated to 450–500° C. This does not neces-

sarily mean that the new complex would not be able to fix phosphate, however.

Two 1-gram samples of kaolinite ground in a 150-gram charge for 5

TABLE 10

THE FIXATION OF PHOSPHATE BY KAOLINITE IN AN EQUILIBRIUM SYSTEM

Reaction		Content of solution*		Content of filtrate		Amount fixed per 100 grams of kaolinite*	
Original solution	Filtrate	K	PO_4	K	PO_4	K	PO_4
pH	*pH*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*
4.56	6.12	38.45	98.55	34.19	79.30	426	1,925
6.66	6.80	52.99	98.55	45.18	87.17	781	1,138
7.70	7.62	71.45	98.55	62.27	95.20	918	335

* A 50-cc portion of solution was shaken with 1 gram of kaolinite.

days in a ball mill were weighed out. One of these was heated to 500° C for 70 hours; the other was left unheated. Each was shaken with a solution of KH_2PO_4 (pH 4.60) containing 98.55 mg of PO_4 for 18 hours, and the amount of PO_4 fixed in each case was determined. There was no appreciable difference in the amount of PO_4 fixed, each fixing approximately 1,000 mg per 100 grams. The loss in weight during the heating period was 0.1345 gram. The pH of the filtrate after fixation in each case was 5.78.

TABLE 11

THE FIXATION OF PHOSPHATE FROM SOLUTIONS HAVING DIFFERENT pH VALUES, BUT WHERE THE K AND PO_4 CONTENTS WERE KEPT CONSTANT

Amount of K in solution	Reaction		Source of K	K fixed per 100 grams of kaolinite	PO_4 fixed per 100 grams of kaolinite
	Solution	Filtrate			
mg	*pH*	*pH*		*mg*	*mg*
183.8	1.87	3.15	None	....	13,776
	1.90	3.07	100 per cent KCl	591±	13,587
	5.41	5.91	60 per cent KCl, 40 per cent KOH	475±	3,068
	6.88	6.83	40 per cent KCl, 60 per cent KOH	423±	2,281
	10.09	8.63	20 per cent KCl, 80 per cent KOH	1,105	619
	12.24	10.51	100 per cent KOH	2,248	None
36.8	1.85	3.05	100 per cent KCl*	162	13,646
	2.31	5.15	100 per cent KOH*	529	9,529

* One-fifth the K content of the others.

In another case where 1 gram of kaolinite was heated at 450–550° C for 50 hours and subjected to shaking for 100 hours in contact with 50 cc of KH_2PO_4 solution (pH 4.43) containing 432.4 mg of PO_4, it fixed 53.6 mg of PO_4 as compared with 67.2 mg fixed by an unheated sample. The pH of the filtrate from the unheated sample was 5.87.

TABLE 12

THE EFFECT OF KH_2PO_4 CONCENTRATION ON PHOSPHATE RETENTION BY KAOLINITE

Reaction*			Content of original solution, per cc		Fixation per 100 grams of kaolinite						Ratio of millimols of PO_4 to milliequivalents of K fixed		
Original solution	Filtrate		K	PO_4	1.0-gram sample		2.5-gram sample		5.0-gram sample		1.0-gram sample	2.5-gram sample	5.0-gram sample
	2.5-gram sample	5.0-gram sample			K	PO_4	K	PO_4	K	PO_4			
pH	*pH*	*pH*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*mg*	*:1.00*	*:1.00*	*:1.00*
4.21	6.30	6.49	10.580	26.344	6,905	18,861	4.411	13.604	2.617	9.629	1.12	1.27	1.51
4.28	Lost	6.39	6.348	15.806	4,737	13.200	2,505	7.274	1.924	5.486	1.15	1.19	1.17
4.32	6.14	6.36	4.232	10.538	......†	8,732	1,662	4.876	1,282	4.061	....	1.21	1.30
4.38	6.25	6.54	2.116	5.269	......†	3,956	1,050	2.634	780	2.315	....	1.03	1.22

* Not determined on the filtrate from the 1.0-gram sample.

† Not determined.

Heating to 500° C, which destroys the crystal structure as revealed by X-ray data, apparently has little effect in reducing the capacity of kaolinite to fix phosphate.

The Effect of Time.—Time (*6, 14, 22*) has been shown to be of considerable importance in phosphate fixation. This was studied by using two

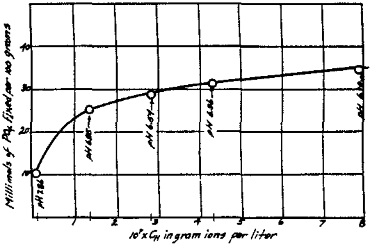

Fig. 4.—The relation between hydrogen-ion concentration of equilibrium solution and phosphate fixed. (Data taken from table 18.)

5-gram samples of finely ground kaolinite suspended in 50 cc of KH_2PO_4 solution. One of the suspensions was shaken for 4 hours and the other for 5 days.

The results are recorded in table 13. The data show very clearly that time is an element of importance in the fixation process, but even so, the fixation after a short exposure is of considerable magnitude.

TABLE 13

The Influence of Time on Phosphate Fixation by Kaolinite

Time of exposure	PO_4 in original solution*	PO_4 in filtrate	PO_4 fixed per 5 grams of kaolinite
	mg	*mg*	*mg*
4 hours	1,242.32	928.72	313.60
5 days	1,242.32	560.22	682.10

* Shaken with 5 grams of kaolinite.

The Effect of Degree of Saturation with Respect to PO_4 on Cation Exchange Capacity.—"Kaolinite phosphates" of different degrees of saturation were made by suspending ground kaolinite in solutions of KH_2PO_4 of different concentrations. After adsorption, the samples were filtered, and the residues were washed with distilled water and air-dried. The degree of phosphate saturation of the kaolinite samples was determined by analyzing the solutions before and after exposure. The base-

exchange capacity of the "kaolinite phosphates" was determined by the usual neutral normal ammonium acetate method used in the Plant Nutrition Laboratory. The results are shown in table 14 and in figure 5.

TABLE 14

THE BASE-EXCHANGE CAPACITY OF "KAOLINITE PHOSPHATES" OF DIFFERENT DEGREES OF PHOSPHATE SATURATION

Material		Exchange capacity		PO_4 fixed per 100 grams
Type	PO_4 per gram	Per 100 grams	Increase per 100 grams	
	mg	*milli-equivalents*	*milli-equivalents*	*millimols*
Kaolinite	0.0	26.85	.....	.....
"Kaolinite phosphate"	14.55	31.92	5.07	15.31
"Kaolinite phosphate"	20.45	34.96	8.11	21.62
"Kaolinite phosphate"	36.37	41.05	14.20	36.29
"Kaolinite phosphate"	64.68	50.68	23.83	68.08

The Effect of the Oxalate Ion on the Adsorption of Phosphate by Kaolinite.—One-gram samples of ground kaolinite were treated with different ratios of 0.1*N* H_3PO_4 to 0.1*N* oxalic acid. The total volume in all cases was 50 cc. The suspensions were shaken for 6 hours and the phosphate and oxalate ions in the filtrates were determined. The oxalate ion

TABLE 15

THE FIXATION OF PHOSPHATE IN THE PRESENCE AND ABSENCE OF THE OXALATE ION

(1 gram of kaolinite used)

H_3PO_4	With oxalate ions present					With no oxalate ions	
	Amount of oxalic acid	Al in solution	Reaction of filtrate	PO_4 fixed per gram of kaolinite	C_2O_4 fixed	Reaction of filtrate	PO_4 fixed per gram of kaolinite
cc	*cc*		*pH*	*mg*	*mg*	*pH*	*mg*
50.0	....	....	....	.....	....	3.42	134.32
37.5	12.5	++	3.28	72.35	?	3.79	105.66
25.0	25.0	+++	3.42	20.21	2.20	4.06	71.63
12.5	37.5	++++	3.13	0.28	None	4.80	34.99
0.0	50.0	+++++	2.52	−0.39	2.20	....	.....

in an H_2SO_4 solution was titrated against standard potassium permanganate. The aluminum content of the filtrates was qualitatively studied.

In another series no oxalic acid was added, but the same amounts of 0.1*N* H_3PO_4 were used as in the various mixtures with the volumes made up by adding distilled water. The filtrates from the latter series contained only a trace of aluminum. A comparison of the results is given in table 15.

In a study of KH_2PO_4 and oxalic acid systems at the same pH values, three different solutions were made to a pH of 4.8–4.9 as follows:

Solution 1.—50 cc of KH_2PO_4 solution + 60 cc distilled water. Solution 2.—50 cc of KH_2PO_4 solution + 50 cc 0.1*N* oxalic acid + 4.6 cc water + 5.4 cc *N* KOH. Solution 3.—50 cc of 0.1*N* oxalic acid + 54.8 cc water + 5.2 cc *N* KOH.

A 1-gram sample of kaolinite was suspended in 50 cc of each of these solutions. The suspensions were shaken for 4 hours and allowed to stand 12 hours before centrifuging. The filtrates were analyzed and the results tabulated (table 16). There was no aluminum present in any of the filtrates, as observed from ammonium hydroxide precipitation.

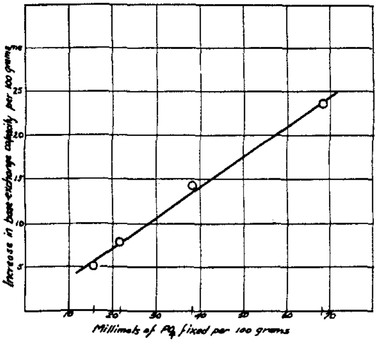

Fig. 5.—The relation of phosphate fixation by kaolinite to increase in base-exchange capacity.

The presence of the oxalate ion decreases the amount of phosphate fixed. In the previous experiment (table 15), this was probably due to the breakdown of the kaolinite (as evidenced by the aluminum in solution) because of the low pH of the initial solution. In the case of the experiment with KH_2PO_4 (table 16), there was no apparent decomposition of the kaolinite, yet there was much less phosphate fixed. The exact reason for the decrease in phosphate fixation is not apparent in this case.

Discussion of Kaolinite Investigations.—Kaolinite when finely ground (table 8) has great capacity to fix phosphate. The hydrogen-ion concentration is an important factor in the fixation process, but since the fixation is of great magnitude in the reaction range of agricultural soils, any soil possessing a kaolinic clay will exhibit this fixing power to a high degree. The fixation decreases as the OH-ion concentration increases

(tables 9, 10, 11, 13); at high pH values (table 11) the kaolinite complex is unable to adsorb phosphate. This is in opposition to cation fixation by kaolinite, which increases with increasing OH-ion concentration.

Since the magnitude of the fixation of phosphate is greatest in the acid range, the H_2PO_4 ion must play a considerable rôle. As indicated by figure 4 and data (table 17) prepared by Buehrer (*4*), as long as the hydrogen-ion concentration is sufficient to permit the presence of the H_2PO_4 ion, phosphate is fixed. At the higher pH values, the increased fixation of K (cation) lowers the pH of the filtrate. When the drop in pH

TABLE 16

THE FIXATION OF PHOSPHATE AND OXALATE IONS FROM SOLUTIONS HAVING AN INITIAL pH OF 4.8–4.9

(1 gram of kaolinite used)

PO_4 added	C_2O_4 added	Fixation per gram of kaolinite		
		PO_4	C_2O_4	K
mg	*mg*	*mg*	*mg*	*mg*
47.85	0.0	13.93	...	4.54
47.85	100.0	7.37	2.2	6.82
0.00	100.0	.....	2.2	Not determined

(increase in hydrogen-ion concentration) is not sufficient to bring about the formation of the H_2PO_4 ion, the magnitude of phosphate fixation is small. Hence, the fixation is roughly proportional to the percentage of H_2PO_4 ions in the solution. The fixation of some phosphate in the pH range of 8 to 10 indicates that HPO_4 ions enter into the process to some extent.

The concentration of the phosphate solution (table 12) has an influence on the degree of phosphate saturation of the kaolinite. The higher the concentration the more nearly saturated will the kaolinite complex become. When a small amount of kaolinite is suspended in a concentrated phosphate solution, it fixes a relatively large amount of the soluble phosphate, while a large amount of kaolinite will fix practically all of the phosphate if the quantity of soluble phosphate is not extremely great. This has a practical application in the use of the phosphate fertilizers on soils having this type of clay.

As the kaolinite complex increases in phosphate content, its base-exchange capacity increases proportionally to the amount of phosphate fixed (table 14 and figure 5). Mattson (*27–30*) showed that phosphated sesquioxides possess a high cation-exchange capacity, and that certain soil colloids possessed this increased exchange capacity when they had adsorbed phosphate. This he attributed to an increase in the acidoid con-

tent of the complex through the adsorption of a polyvalent ion. The data in table 14 substantiate the results of Mattson. Since the data further indicate the importance of the H_2PO_4 ion and HPO_4 ion at the higher pH values, one of the possible reactions is as follows: $3\ CH_3\ COONH_4 + HO\ [Si(OH)_mAl]\ H_2PO_4 \rightarrow NH_4O\ [Si(OH)_mAl]\ (NH_4)_2PO_4 + 3\ CH_3COOH$. The $(OH)_m$ designates OH groups which are nonreactive under the prevailing conditions.

When the pH of the extracting solution is somewhere below pH 1.5–2.0 and the ratio of solution to kaolinite is great (mass action), the kaolinite

TABLE 17

CONCENTRATION OF PHOSPHATE IONS IN SOLUTION AT VARIOUS HYDROGEN-ION CONCENTRATIONS BASED ON AN ASSUMED TOTAL CONCENTRATION OF 1 PART PER MILLION* OF PO_4

pH	H_3PO_4	H_2PO_4-	$HPO_4=$	$PO_4\equiv$
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*
3	0.084	0.92	......†	......†
4	.0091	.99	0.0019	......
5	.00089	.98	.0194	......
6	0.00076	.79	.164	......
7	.......†	.33	.66	......
8	....	.048	.94	......
9	....	0.00495	.98	0.00035
10	....	......†	0.99	0.0035

* From Buehrer (*4*).

† The blank spaces denote insignificant values for the purpose involved.

begins to break down, and as a result, its ability to fix phosphate decreases. When the pH approaches a value of 1, there is a complete loss of ability to fix phosphate. This effect was produced when a 1-gram sample of kaolinite was shaken for 10 hours with 50 cc of HCl of pH 1.2. The filtrate had a high aluminum content. The residue fixed very little phosphate, either from a solution of H_3PO_4 (pH 1.9), or from a solution of KH_2PO_4 (pH 4.3). Before treating with the HCl, a sample of the original kaolinite fixed between 140 and 160 mg of PO_4 per gram. Apparently a breakdown of the kaolinite took place in the oxalic-acid and H_3PO_4 series. The initial acidity was such that it broke down some of the kaolinite and prevented as much fixation as occurred when only H_3PO_4 of pH 1.9 was used. The oxalic acid had a pH of 1.6 and the pH of the H_3PO_4 and oxalic acid mixtures must have been somewhere between these values.

Decomposition also occurs when the concentration of OH ion becomes sufficient. A 0.1*N* NaOH solution decomposes kaolinite to a slight extent. When the KOH and 0.1*N* H_3PO_4 mixture (pH 12.2) was used with

kaolin, a slight decomposition occurred, as evidenced by the fact that a small amount of aluminum went into solution. The equilibrium pH was 10.51. No aluminum was found in the filtrate from the KCl–KOH–H_3PO_4 (pH 10.0) treatment of kaolinite. In this case, however, the final pH dropped to 8.0. The data indicate that a wide ratio of solution to kaolinite and pH values of 10 or above are necessary before there is any appreciable decomposition on the alkaline side. The data indicate that the decomposition of kaolinite occurs at pH values outside the range for agricultural soils or for plant growth. Furthermore, any phosphate the kaolinite fixes, especially from a phosphate solution of low concentration (which would be the case in the soil even with liberal phosphate fertilization), is of low availability for plant use.

The exact effect of the oxalate ion is not clear. Russell and Prescott (*42*) found that dilute acids removed phosphates from a soil in the following order: $0.1N$ oxalic $>$ $0.1N$ citric $>$ $0.1N\ H_2SO_4 > 0.1N\ HNO_3 = 0.1N\ HCl$; and that soils adsorbed phosphorus from sodium phosphate readily in the presence of HCl and HNO_3 but to a notably less extent in the presence of an equivalent concentration of citric acid. They infer that acids like citric and oxalic satisfy the adsorption capacity of the soil and leave it with little power to take up phosphoric acid. Demolon and Bastisse (*8*) found that the presence of citrate and oxalate ions reduced the amount of P_2O_5 fixed by a soil. No data were presented to show the fixation of the citrate or oxalate ions though a partition of these ions to the phosphate ion was given as a reason for the lower power to fix phosphate. Lichtenwalner, Plenner, and Gordon (*25*) found that citric acid had no effect in removing phosphate which had been fixed by an iron hydrogel, but it peptized the aluminum hydrogel and removed some adsorbed phosphate from the latter. Weiser (*49*) reported that organic matter was apparently effective in deactivating iron- and aluminum-fixing materials.

The data presented in tables 15 and 16 substantiate the above observations that the presence of oxalate ions (or organic matter) reduce phosphate fixation, but they do not substantiate a strict stoichiometric relation in the fixation process.

COMPARISON OF KAOLINITE WITH OTHER CLAY MATERIALS

One-gram samples of kaolinite and H-bentonite were shaken intermittently for 1 week with 50 cc KH_2PO_4 solution containing 98.55 mg of PO_4. The suspensions were centrifuged, and the clear filtrates were analyzed. One-gram Volclay[9] samples were shaken continuously on a

[9] Volclay is a trade name for bentonite found near Belle Fourche, S. D., and supplied by the American Colloid Company.

roller for 24 hours with a similar solution and allowed to stand 2 days before being centrifuged.

TABLE 18

THE FIXATION OF PHOSPHATES BY DIFFERENT CLAY MATERIALS

Reaction*		PO_4 fixed per 100 grams of kaolinite	PO_4 fixed per 100 grams of H-bentonite	PO_4 fixed per 100 grams of Volclay
Original solution	Kaolinite filtrate			
pH	*pH*	*mg*	*mg*	*mg*
4.54	6.10	3,384	1,510	689
6.08	6.36	3,056	1,407	...
6.38	6.54	2,759	1,305	.
6.75	6.85	2,452	1,407	516
9.22	7.86	986	762	295

* The pH of the H-bentonite and Volclay filtrates was not determined.

The data on fixation are given in table 18. Apparently kaolinite has a much higher capacity for fixing phosphate than has bentonite. Soils in which the clay is of a kaolinic character would therefore require a higher rate of phosphate fertilization in order to give increased yield if the kaolinite is finely divided.

GREENHOUSE TESTS OF PHOSPHATE FERTILIZER ON AIKEN CLAY LOAM

The Effect of Rate and Placement.—Two different rates of application of superphosphate were used in these experiments—280 pounds and 2,800 pounds per acre. Each 2-gallon glazed earthenware pot contained 8,000 grams of Aiken clay loam. No drainage was allowed to occur from the pots. In one series the phosphate was thoroughly mixed with all of the soil; and in the other series it was mixed with the upper 3,000 grams. The phosphate was applied only once, at the beginning of the experiment. At each planting date, 25 cc of *M* $Ca(NO_3)_2$ and a like amount of *M* KNO_3 were added to each pot. Tomatoes, barley, and vetch were used as the major crops, with buckwheat introduced in cases where the other crops were failures or did not seem to be giving much growth. All treatments were in triplicate.

The plants were harvested when the first blossoms appeared. Only the tops of the plants were used in determining the phosphate removed. The roots were left in the soil.

Tomatoes were a failure with the lower application of phosphate, and barley did not grow very well; hence, buckwheat was substituted later. From the data (table 19), buckwheat appears to be able to do much better than either tomatoes or barley. This is in accord with general field

observations. All of the crops were able to make a fair growth when the rate of application of superphosphate was 2,800 pounds per acre. In a general way, the data bear out the conclusion that the efficiency of superphosphate is slightly higher where locally placed in the soil. The results also show that for some crops a nominal application of superphosphate (280 pounds per acre) on this soil is valueless, and to get response for

TABLE 19
THE RECOVERY OF PHOSPHATE FROM AIKEN CLAY LOAM BY VARIOUS CROPS
(Averages of triplicate treatments)

P applied	Crop sequences*	P recovered		Total P recovered	
		Major crop	Buckwheat	Amount	Percentage†
mg		*mg*	*mg*	*mg*	*per cent*
0	T T Bu Bu	0.07	4.98	5.05	.....
	B B B Bu	1.61	1.28	2.89	.....
	V V V V	10.38	.....	10.38	.....
125.75 mixed throughout soil	T T Bu Bu	0.19	9.51	9.70	3.70
	B B B Bu	15.62	16.00	31.62	22.85
	V V V V	28.46	.....	28.46	14.38
125.75 in upper layer	T T Bu Bu	0.49	11.68	12.17	5.66
	B B B Bu	11.57	9.47	21.04	14.43
	V V V V	31.08	.....	31.08	16.46
1,257.5 mixed throughout soil	Tomatoes (4 crops)	76.54	.....	76.54	6.08
	Barley (4 crops)	67.80	.....	67.80	5.22
	Vetch (4 crops)	105.19	.....	105.19	7.54
1,257.5 in upper layer	Tomatoes (4 crops)	134.65	.....	134.65	10.70
	Barley (4 crops)	109.80	.....	109.80	8.56
	Vetch (4 crops)	119.92	.....	119.92	8.71

* T = Tomatoes, B = Barley, V = Vetch, and Bu = Buckwheat.

† The percentage recovery is calculated after deducting the amount of phosphorus present in crops grown on unfertilized soil; in the case of 4 crops of tomatoes or barley, the deduction is based on the assumption that the recovery by 4 crops is proportionate to that by 2 or 3 crops.

these crops, large applications must be made. Investigations (*43*) have shown that for certain soils small applications of soluble phosphate fertilizers give no response, while a much higher rate of application often gives good results.

The Effect of Soil Reaction.—The reaction of the Aiken clay loam was modified by the use of dilute H_2SO_4, $CaCO_3$, and Na_2CO_3. The $CaCO_3$ and Na_2CO_3 were mixed with the soil by rolling the soil back and forth several times. The dilute H_2SO_4 was sprayed on thin layers of the soil; after which the soil was allowed to come to equilibrium with the acid. The acidulation process was repeated until the equilibrium mixtures had the desired pH. Triple superphosphate at the rate of 2,800 pounds per acre was thoroughly mixed with the soil. This was equivalent to

3,142 mg of phosphorus per 2-gallon pot holding 8,000 grams of soil. All treatments were in triplicate.

TABLE 20

THE EFFECT OF REACTION ON THE RECOVERY OF APPLIED PHOSPHATE TO AIKEN CLAY LOAM

(Averages of triplicate treatments)

Reaction of soil	Tomatoes*			Barley*			Vetch*		
	Total yield	P recovered		Total yield	P recovered		Total yield	P recovered	
		Amount	Per cent†		Amount	Per cent†		Amount	Per cent†
pH	*grams*	*mg*	*per cent*	*grams*	*mg*	*per cent*	*grams*	*mg*	*per cent*
4.0	0.00	......	....	0.00	......	....	0.00	.....	...
5.0	44.59	93.71	2.98	46.66	129.21	4.11	17.09	36.21	1.15
5.4	76.95	145.90	4.64	31.77	88.65	2.82	16.81	42.55	1.35
6.0‡	74.75	166.12	5.29	72.75	165.61	5.27	32.47	65.90	2.10
7.8									
$CaCO_3$§	70.53	158.17	5.03	66.93	163.80	5.21	26.54	57.34	1.82
Na_2CO_3¶	36.14	81.12	2.58	73.07	131.94	4.20	12.11	30.89	0.98

* In all cases, except for tomatoes in the pH 5.4 series, 3 crops were grown. In the exception noted, only 2 crops were grown during the period of the experiment.

† On the basis of 3,142 mg of phosphorus added per pot. No deductions were made for the soil, since other experiments indicated that this amount was negligible.

‡ Natural soil. § 80 grams per pot. ¶ 400 cc *M* Na_2CO_3 per pot.

Where Na_2CO_3 was used, the soil had an undesirable physical condition which tended to prevent water penetration. As a result, aeration was deficient, especially after the addition of moisture to the soil. The data in general (table 20) indicate that within the reaction range suitable for crop production, there is little to choose. Apparently a reaction between pH 6 and pH 7 is most satisfactory, and nothing would be gained in the Aiken clay loam by changing the present soil reaction.

TABLE 21

THE EFFECT OF SOURCE OF NITROGEN ON THE RECOVERY OF PHOSPHORUS FROM TRIPLE SUPERPHOSPHATE BY TOMATOES

(Averages of triplicate treatments)

Treatment	Yield			Total P recovered	
	First crop	Second crop	Third crop	Amount	Per cent*
	grams	*grams*	*grams*	*mg*	*per cent*
Triple superphosphate only	23.72	3.44	4.82	107.02	3.41
Triple superphosphate + $(NH_4)_2SO_4$	34.66	26.02	7.72	156.13	4.97
Triple superphosphate + $Ca(NO_3)_2$	36.91	29.92	11.76	159.91	5.09

* On the basis of 3,142 mg of phosphorus added per pot. No deductions were made for that furnished by the soil without fertilization since other experiments indicated this was negligible.

The Effect of Source of Nitrogen.—Triple superphosphate at the rate of 2,800 pounds per acre was thoroughly mixed with virgin Aiken clay

loam. This was equivalent to 3,142 mg of phosphorus per 2-gallon pot holding 8,000 grams of soil. In some cases, the nitrogen was supplied as $(NH_4)_2SO_4$, and in others as $Ca(NO_3)_2$. At the beginning of growth at each planting date, 25 cc of *M* $(NH_4)_2SO_4$ or $Ca(NO_3)_2$ was added. All treatments were in triplicate. Tomatoes were grown on the soil.

TABLE 22

THE EFFECT OF A GOOD STARTING MEDIUM ON PHOSPHATE REMOVAL BY TOMATOES
(Averages of triplicate treatments)

Series	Medium of growth*	Yield			P in crops
		First crop	Second crop	Third crop	
		grams	*grams*	*grams*	*mg*
1	5,000 grams Aiken clay loam beneath 3,000 grams Fresno	22.91	16.42	9.64	89.64
2	5,000 grams sand† beneath 3,000 grams Fresno fine sandy loam	14.50	10.37	3.22	56.08
3	8,000 grams Aiken clay loam	0.02	0.05	0.05	0.10
4	8,000 grams Fresno fine sandy loam	25.29	26.96	14.82	178.92

* Each pot received 25 cc of *M* $Ca(NO_3)_2$ applied to the surface at each planting date.

† At the beginning of the experiments and at the beginning of each succeeding cropping period, 500 cc of a solution 0.005 *M* in $Ca(NO_3)_2$, 0.005 *M* in KNO_3, and 0.002 *M* in $MgSO_4$ were added to the sand; 2 cc of iron tartrate were also added.

Where the triple superphosphate was used alone, the foliage had a yellow color, which indicates nitrogen deficiency, especially after the first period. Even the first crop showed some nitrogen deficiency. The influence of the triple superphosphate extended over two cropping periods where the nitrogen deficiency was corrected (table 21), but beyond this the applied phosphate had little effect. The third crop in all cases was very spindly and showed phosphate deficiency. No choice can be made between the use of $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ as the source of nitrogen with triple superphosphate on this soil.

TABLE 23

THE RECOVERY BY TOMATOES OF PHOSPHORUS SUPPLIED TO AIKEN CLAY LOAM BY SUPERPHOSPHATE OF DIFFERENT PARTICLE SIZES
(Averages of duplicate treatments)

Size of particle	Oven-dry weight of crops	Applied phosphorus recovered by plants	Ratio to granulated superphosphate
	grams	*per cent*	*:1.00*
Granulated superphosphate	26.13	7.32	1.00
Up to 10 mesh	40.45	16.22	2.21
10 to 20 mesh	33.07	11.95	1.63
20 to 60 mesh	21.80	5.90	0.80
60 to 100 mesh	18.75	5.09	0.69
100 to 200 mesh	10.89	2.31	0.31
Finer	11.65	3.23	0.44

The Effect of a Good Starting Medium.—Three crops of tomatoes were grown in pots containing a total of 8,000 grams of Fresno fine sandy loam, Aiken clay loam, or combinations of these with each other or with sand. Series 1 consisted of 5,000 grams of Aiken clay loam placed in the bottom of the pot; on top of and unmixed with this were 3,000 grams of

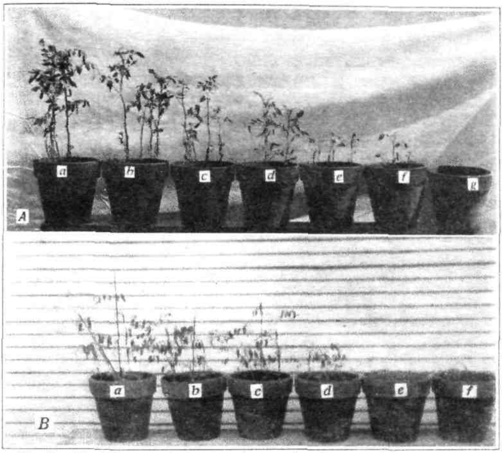

Fig. 6.—The influence of the size of superphosphate particles on the growth of tomatoes on Aiken clay loam: *A*, second crop; *B*, sixth crop. The size of particles of superphosphate applied to the various pots was as follows: *a*, coarser than 10 mesh; *b*, 10–20 mesh; *c*, 20–60 mesh; *d*, 60–100 mesh; *e*, 100–200 mesh; *f*, finer than 200 mesh. In series *A*, pot *g* contained Aiken soil with no phosphate.

Fresno soil. Series 2 consisted of 5,000 grams of acid-washed white sand in the bottom of the pot; on top of and unmixed with this were 3,000 grams of Fresno soil. Series 3 was Aiken soil only. Series 4 was Fresno soil only. The Fresno and Aiken soils contained 0.16 per cent and 0.18 per cent of total PO_4 respectively. All treatments were in triplicate.

The tomato plant was unable to make any growth on the Aiken soil, but it made a nice growth on the Fresno soil (table 22). The root systems were extensive both in the Aiken soil below the Fresno soil and in the sand below the Fresno soil; more phosphorus was recovered from the plants on the former than on the latter, but just how much of the extra

phosphorus was taken from the Aiken soil cannot be determined from these data. The results indicate that if the plant is given a good start, it can probably secure more phosphorus than it normally does from unfertilized virgin Aiken soil.

The Effect of Size of Superphosphate Particles.—Aiken clay loam in 7,000-gram lots was placed in 10-inch pots and 2.8 grams of superphosphate of various-sized particles were thoroughly mixed in the upper 2,000 grams of soil. Nitrogen was supplied in the form of $Ca(NO_3)_2$ and KNO_3 before planting each crop. Seven consecutive crops of tomatoes were grown in each pot without any further phosphate treatment. Treatments were in duplicate.

Table 23 gives the condensed results. They indicate clearly that coarse particles are to be preferred over fine particles of superphosphate for such soils (fig. 6).

GREENHOUSE TESTS OF COMPARATIVE VALUE OF SUPERPHOSPHATE AND "KAOLINITE PHOSPHATES"

Samples of ground kaolinite were treated with different strength solutions of KH_2PO_4. After several hours of shaking, the kaolinite complex was thoroughly washed with distilled water to remove any occluded phosphate, and the PO_4 content of all of the leachates was determined. The difference between the PO_4 in the original solution and that found in the leachate was considered as fixed phosphate. The term "kaolinite phosphate" is used to designate the phosphated kaolinite. Three different degrees of saturation were secured with kaolinite treated as given above. These were used in sand cultures and compared with the phosphorus furnished by 1 gram of superphosphate. The amount of phosphorus furnished in all cases was made equivalent to that in the superphosphate by adjusting the amount of phosphated kaolinite. Each pot held 5,000 grams of pure sand. The phosphate was thoroughly mixed throughout the sand. To each container, after planting tomato seed, was added 800 cc of Hoagland's solution minus PO_4. Five plants were allowed to grow in each pot. The growth period was of 45 days' duration (January 7 to February 21, 1938). The plants grown on the superphosphate treatment were in bloom at the time of harvest. The oven-dry weights of the plants were as follows:

Phosphate used	Total weight of plants, *grams*
Superphosphate	8.10
"Kaolinite phosphate," 64.0 mg PO_4 per gram	2.40
"Kaolinite phosphate," 36.0 mg PO_4 per gram	0.95
"Kaolinite phosphate," 14.5 mg PO_4 per gram	0.45
None	0.14

The comparative growth with the various treatments is shown in figure 7.

The data indicate that the availability of the adsorbed phosphate varies with the degree of saturation of the adsorbed complex. If a light

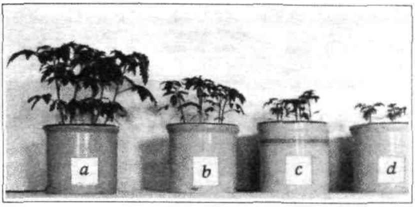

Fig. 7.—The comparative growth of tomatoes in sand cultures where the phosphorus is furnished as: *a*, superphosphate; *b*, strongly saturated "kaolinite phosphate"; *c*, medium-saturated "kaolinite phosphate"; *d*, weakly saturated "kaolinite phosphate."

fertilizer application is made on a soil, the phosphate of which is controlled by the kaolinite complex, there will be practically no response by certain crops. Only when the kaolinite is more highly saturated will the plant be able to secure its needed phosphate for growth, and even then the growth period must be of considerable length in order to secure full development of the plant.

GREENHOUSE TESTS OF THE EFFECT OF VARIOUS COLLOIDS ON SUPERPHOSPHATE EFFICIENCY

Greenhouse experiments were conducted with sand mixtures and Aiken clay loam mixtures in Mason quart jars. The total air-dry weight of material in each jar was 1,250 grams except in the case of the Aiken soil, where it was 860 grams. The treatments were conducted in duplicate. The colloid and superphosphate were thoroughly mixed in the jar. The kaolinite used in the 1 per cent mixture had been ground in a ball mill for 7 days. The Volclay was 200-mesh material. The Aiken colloid had been pulverized in a mortar until it was quite fine. Natural Aiken clay loam was used without any previous treatment. One tomato plant was grown per jar. At the beginning of the experiment, 200 cc of Hoagland's solution minus PO_4 was added to each jar.

The results (table 24 and fig. 8) fully justify the conclusion that kaolinic clays are very effective in fixing phosphates in a form not readily

accessible to plants when limited amounts of soluble phosphates are applied. On the other hand, a soil containing montmorillonitic (bentonitic) clay should be more effective in supplying plants with their needed phosphate. The plants in the sand culture were in bloom when harvested.

TABLE 24

EFFECT OF VARIOUS COLLOIDS ON GROWTH OF TOMATOES WITH VARIOUS ADDITIONS OF SUPERPHOSPHATE

Culture	Superphosphate additions*				
	None	50 mg	100 mg	150 mg	200 mg
	Average total oven-dry weight of tomato plants				
	grams	*grams*	*grams*	*grams*	*grams*
Sand only	0.02	1.00	1.60	1.80	1.75
Sand + 1 per cent Volclay	0.02	1.45	1.45	1.40	1.50
Sand + 1 per cent Aiken colloid	0.01+	0.13	0.90	1.42	1.65
Sand + 20 per cent crushed kaolinite	0.02	0.02	0.02	0.02+	0.04
Sand + 1 per cent finely divided kaolinite	0.01	0.01+	0.02	0.03	0.03
Aiken clay loam	0.01	0.01+	0.02	0.03	0.03

* Considering the volume weights of sand and Aiken clay loam, these applications of superphosphate are approximately equivalent to 80, 160, 240, and 320 pounds per acre, respectively.

DISCUSSION OF RESULTS

Certain soils contain colloidal material which by X-ray pattern analysis has been shown to be kaolinic in character. Other investigations, where X-ray facilities have not been available, have shown the colloidal fraction of a great many soils to have a low silica : sesquioxide ratio, suggesting the presence of a kaolinic type of clay. These soils are known to have a high capacity to fix soluble phosphate fertilizers in forms not readily available for plants. Since most of these soils are red in color, they have been assumed to be high in iron. In some cases this is actually the case, but in others the iron content is not so great as the color of the soil would indicate. Iron has been considered the chief factor in the phosphate-adsorbing system of these soils. Certain results render such an assumption questionable.

The presence of free ionic iron in any appreciable amount in the soil occurs only under extreme conditions of soil reaction. Much the same may be said of aluminum. Experiments show (curve *b* in figs. 1 and 2, pp. 348 and 349) that iron phosphate formed by these ions would be removed from solutions within the usual reaction range of soils. But such experiments do not prove that ionic iron is present in soils to fix applied soluble phosphates rapidly; and hence, do not give the real picture of existing soil conditions.

Iron and aluminum hydrosols and hydrogels are known to have the ability to remove soluble phosphates from solution under certain conditions (curve *a* in figs. 1 and 2). Hydrolysis of the freshly prepared iron complexes occurs, however, and at pH 6 and above there is a considerable release of PO_4 even in the presence of an excess of iron. The PO_4 released under these conditions by the hydrosol is much greater than that present

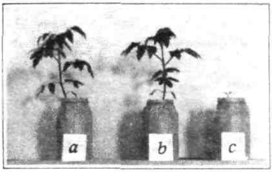

Fig. 8.—The comparative growth of tomatoes as influenced by phosphate availability in: *a*, sand only + 200 mg superphosphate; *b*, sand + 1 per cent Volclay + 200 mg superphosphate; *c*, sand + 1 per cent kaolinite + 200 mg superphosphate. (Other nutrients were derived from Hoagland's solution minus PO_4.)

in the soil solution under similar conditions, and is not in accord with the ability of plants to grow on such soils. Other factors must, therefore, be involved.

The experiments with a good grade of kaolinite as shown by X-ray pattern data (fig. 3, p. 357) indicate that this material has a high phosphate-fixing power when ground in a ball mill for a few days. The clay particles of soils are colloidal in nature and it is permissible to assume that at least some of the kaolinite is colloidally dispersed. Russell (*41*) states that under natural conditions kaolinite is not so finely divided as some of the other clay minerals. The data in table 8 (p. 357) indicate that a soil weighing 2,000,000 pounds per surface 6 inches in depth and containing 1 per cent of finely divided kaolinite would be able to fix 2,058 pounds of PO_4 under conditions similar to those in the experiment.

The fixation by kaolinite is extremely high for all concentrations of soluble phosphates in the reaction range of agricultural soils. However, the product formed varies in phosphate saturation according to the concentration (amount of phosphate per unit volume of solution) of phosphate at its disposal. When these "kaolinite phosphates" of different degrees of saturation are used as a source of phosphate for plants in pot cultures, the response is directly proportional to the degree of satura-

tion. This means that where this kind of adsorbing system is controlling the phosphate equilibrium in the soil, a small application is ineffective; and to secure results, a much higher rate of phosphate application must be employed.

The fixation is greatest at acid reactions. When the exposed solution contains H_2PO_4 ions, the fixation is great. This has a very important bearing, because experiments (*23, 32*) indicate that this phosphate ion is the one which plants absorb most rapidly. If the colloidal system of the soil prefers this kind of ion for fixation, soils having this kind of adsorbing system are extremely efficient in "competing" with the plant for phosphorus. As a result, the plant, because of its limited root area, is at a great disadvantage and suffers because of this competition.

Decomposition data indicate that the valences necessary for the fixation depend upon aluminum. When the reaction is such that much aluminum appears in solution, the fixation of phosphate by the kaolinite is decreased. This, however, does not take place in the usual soil reaction range and although of theoretical value in determining the nature of the fixation is not of practical agricultural interest. When the concentration of the OH ion is increased, less and less phosphate is fixed. When the OH ion concentration attains a certain strength, somewhere above pH 10, there is little or no more fixation; but an actual breakdown of the clay complex occurs. Likewise, if the H ion concentration is increased sufficiently, somewhere below pH 2, decomposition occurs, as would be expected from the use of strong acids in general analytical work. Between these extremes, the phosphate fixed increases with a decrease in pH, and cation fixation decreases.

Colloids having a high silica : sesquioxide ratio have a lower capacity to fix phosphates, as shown by both chemical and greenhouse work. This is in general accord with the work of other investigators.

Gile (*18*) found in studying the influence of various soil colloids on the efficiency of superphosphate that soils having colloids of low silica : sesquioxide ratios depressed the efficiency more than those having a higher ratio. Furthermore, the colloids which depressed superphosphate most were those of smallest base-exchange capacity. These properties suggest that the high phosphate-fixing colloids studied by Gile were kaolinic in character.

Kaolin is formed by weathering processes (*39*) and is probably present in some of its forms in all soils containing colloids of a low silica : sesquioxide ratio. Not only have such soils, therefore, active sesquioxides in more or less abundance, but also the kaolin in them is in a highly divided state as a result of the pronounced weathering, which augments phos-

phate retention greatly. The presence of kaolin in this condition severely handicaps the ability of plants to secure phosphorus either from the supply in the soil itself or from that of applied soluble phosphates, which are rapidly converted into a highly inaccessible form.

The other clay minerals studied exhibit less fixing power, but even so their presence in soils is an important contributing factor to phosphate fixation. According to our investigations, the efficiency of applied soluble phosphates is a function of the kind of clay minerals present in the soil: if the clay is kaolinlike, a low efficiency is inevitable, while soils with a montmorillonitic clay complex will have a higher degree of phosphate efficiency.

Coarsely ground superphosphate is better than finely divided superphosphate for these kaolinic soils. There are two reasons for this: First, such material is less rapidly fixed in the soil; second, the fixed phosphate is in more highly saturated zones, and as such, is of higher availability than it would be if it were fixed from finer phosphate particles, where the concentration of the solution surrounding the clay is lower. The first reason accounts for the better results in the first crops, and in all probability the later crops are benefited largely because of the second factor. Local application also would have produced more highly saturated colloids.

SUMMARY

Soils with a kaolinic type of clay have a high capacity to fix soluble phosphates, as is shown by both chemical and greenhouse experiments. This is in accord with field results.

Phosphate fixation by the various iron systems alone is not considered sufficient to account for all of the properties that these soils show with respect to phosphate availability.

Kaolinite when ground to colloidal dimensions has a high phosphate-fixing capacity.

The fixation is greatest at acid reactions, which indicates that the H_2PO_4 ion is the most favored phosphate ion for the reaction.

An increase in base-exchange capacity accompanies the increase in phosphate fixed.

Greenhouse experiments show that the availability of the phosphate in "kaolinite phosphate" is directly proportional to the degree of phosphate saturation. This is taken to indicate that a light phosphate fertilizer application would be ineffective on soils having a kaolinic kind of clay.

Even a very low percentage of kaolinite, if in a colloidal condition in a soil, will tie up phosphate and make it unavailable for plants.

Greenhouse results substantiate the laboratory data in showing that bentonite (Volclay) has a much lower capacity to fix phosphorus in an inaccessible form for plant growth than does colloidal kaolinite.

The results are considered sufficient to explain why soils with a kaolinic type of clay have a high capacity to fix phosphate and a low phosphate availability as measured by plant growth.

ACKNOWLEDGMENTS

The writer wishes to express his gratitude for assistance rendered by all the members of the committee in charge of the thesis, and especially to Professors J. S. Burd and D. R. Hoagland for their many kindly criticisms and suggestions during the progress of the work. An indebtedness to Professor W. H. Dore for the X-ray work necessary in producing figure 3 is also gratefully acknowledged.

LITERATURE CITED

1. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.
1930. Official and tentative methods of analysis. 564 p. Washington, D. C.

2. BRADFIELD, RICHARD.
1931. The colloidal chemistry of soils. p. 569–90. *In:* Alexander, Jerome. Colloid chemistry. vol. 3. The Chemical Catalog Co., Inc., New York, N. Y. (Original not read; reported by Scarseth, *44*.)

3. BROWN, I. C., and H. G. BYERS.
1932. The fractionation, composition, and hypothetical constitution of certain colloids derived from the great soil groups. U. S. Dept. Agr. Tech. Bul. **319**:1–43.

4. BUEHRER, T. F.
1932. The physico-chemical relationships of soil phosphates. Arizona Agr. Exp. Sta. Tech. Bul. 42:155–212.

5. COMBER, N. M.
1925. The rôle of the electronegative ions in the relations between soils and electrolytes. Faraday Soc. Trans. **20**:1–6.

6. DAVIS, L. E.
1935. Sorption of phosphates by non-calcareous Hawaiian soils. Soil Sci. **40**: 129–58.

7. DEAN, L. A.
1934. Electrodialysis as a means of studying the nature of soil phosphates. Soil Sci. 37:253–66.

8. DEMOLON, A., and E. BASTISSE.
1934. Contribution a l'etude de la mechanique chimique des anions dans le sol. Ann. Agron. n. s. **4**:53.

9. DOUGHTY, J. L.
1931. Phosphorus studies in Alberta soils. Scientific Agr. **12**:43–51.

10. ELLETT, W. B., and H. H. HILL.
1917. A ten-year study of the effect of fertilizers on the soluble plant food in the soil and on the crop yield. Virginia Agr. Exp. Sta. Tech. Bul. **13**: 46–72.

11. FISHER, E. A.
1922. The phenomena of absorption in soils: a critical discussion of the hypotheses put forward. Faraday Soc. Trans. 17:305–16.

12. FORD, M. C.
1932. The distribution, availability, and nature of the phosphates in certain Kentucky soils. Jour. Amer. Soc. Agron. **25**:395–410.

13. FORD, M. C.
1933. The nature of phosphate fixation in soils. Jour. Amer. Soc. Agron. **25**:134–44.

14. FRAPS, G. S.
1922. The fixation of phosphoric acid by the soil. Texas Agr. Exp. Sta. Bul. **304**:1–22.

15. Gaarder, T., and O. Grahl-Nielsen.
1936. *Die Bindung der Phosphorsaure in Erdboden: II. Untersuchungen aus Westnorwegen. Vestl. Fors. Forsksstation.* Meddl. (Bergen) 5(4) (NR 18):1–109.

16. Ghosh, J. C., and P. B. Bhattacharyya.
1930. Removal of ions from solutions of calcium dihydrogen phosphate by treatment with hydrous gels of alumina, silica, and their mixtures. Soil Sci. 29:311–22.

17. Gilbert, B. E.
1931. The Forty-third Annual Report of the Director of the Rhode Island Agricultural Experiment Station. Rhode Island State College Bul. 26: 28–49. (See especially p. 40.)

18. Gile, P. L.
1933. The effect of different colloidal soil materials on the efficiency of superphosphate. U. S. Dept. Agr. Tech. Bul. 371:1–49.

19. Gordon, N. E., and E. B. Starkey.
1922. Influence of soil colloids on availability of salts. Soil Sci. 14:1–7.

20. Harrison, W. H., and S. Das.
1921. The retention of soluble phosphates in calcareous and noncalcareous soils. India Dept. Agr. Memoirs Chem. Series 5:195–236.

21. Heck, A. P.
1934. Phosphate fixation and penetration in soils. Soil Sci. 37:343–55.

22. Hibbard, P. L.
1935. Factors influencing phosphate fixation in soils. Soil Sci. 39:337–58.

23. Hoagland, D. R., and A. R. Davis.
1929. The intake and accumulation of electrolytes in plant cells. Protoplasma 6:610–26.

24. Kelley, W. P., and W. H. Dore.
1937. The clay minerals of California soils. Soil Science of America Proc. 2:115–20.

25. Lichtenwalner, D. C., A. L. Plenner, and N. E. Gordon.
1923. Adsorption and replacement of plant food in colloidal oxides of iron and aluminum. Soil Sci. 15:157–65.

26. Marais, J. S.
1922. The comparative agricultural value of insoluble mineral phosphates of aluminum, iron, and calcium. Soil Sci. 13:355–409.

27. Mattson, S.
1927. Anionic and cationic adsorption by soil colloidal materials of varying $SiO_2/Al_2O_3 + Fe_2O_3$ ratio. First Internatl. Cong. Soil Sci. [Washington] Proc. 2(Comm. II):199–211.

28. Mattson, S.
1930–1931. Laws of soil colloidal behavior: III and IV. Isoelectric precipitates. Soil Sci. 30:459–95; 31:57–77.

29. Mattson, S.
1931. Laws of soil colloidal behavior: V. Ion adsorption and exchange. Soil Sci. 31:311–31.

30. MATTSON, S.
1931. Laws of soil colloidal behavior: VI. Amphoteric behavior. Soil Sci. 32: 343–65.

31. MATTSON, S., and A. J. PUGH.
1934. Laws of soil colloidal behavior: XIV. The electrokinetics of hydrous oxides and their ionic exchange. Soil Sci. 38:299–313.

32. MCGEORGE, W. T., and J. F. BREAZEALE.
1932. Studies of iron, aluminum, and organic phosphates and phosphate fixation in calcareous soils. Arizona Agr. Exp. Sta. Tech. Bul. 40:59–111.

33. PUGH, A. J.
1934. Laws of soil colloidal behavior: I. Aging of colloids and base exchange. Soil Sci. 37:403–27.

34. PUGH, A. J.
1934. Laws of soil colloidal behavior: II. Ionic exchange with hydroxides. Soil Sci. 38:161–73.

35. PUGH, A. J.
1934. Laws of soil colloidal behavior: III. Colloidal phosphates. Soil Sci. 38: 315–34.

36. PUGH, A. J., and M. S. DU TOIT.
1936. The composition and ionic exchange of ferric silicates and phosphates. Soil Sci. 41:417–31.

37. RAVIKOVITCH, S.
1934. Anion exchange: I. Adsorption of the phosphoric acid ions by soils. Soil Sci. 38:219–39.

38. RAVIKOVITCH, S.
1934. Anion exchange: II. Liberation of the phosphoric acid ions adsorbed by soils. Soil Sci. 38:279–90.

39. ROSS, C. S., and P. F. KERR.
1931. The kaolin minerals. U. S. Geol. Survey Prof. Paper 165E:151–76.

40. ROSZMANN, C. A.
1927. Retention of phosphorus by soil colloids. Soil Sci. 24:465–74.

41. RUSSELL, E. J.
1937. Soil conditions and plant growth. 7th ed. 655 p. Longmans, Green and Co., New York, N. Y.

42. RUSSELL, E. J., and J. A. PRESCOTT.
1916. The reaction between dilute acids and the phosphorus compounds of the soil. Jour. Agr. Sci. 8:65–110.

43. SCARSETH, G. D.
1932. Morphological, greenhouse, and chemical studies of the Black Belt soils of Alabama. Alabama Agr. Exp. Sta. Bul. 237:1–48.

44. SCARSETH, G. D.
1935. The mechanism of phosphate retention by natural alumino-silicate colloids. Jour. Amer. Soc. Agron. 27:596–616.

45. STARKEY, E. B., and N. E. GORDON.
1922. Influence of hydrogen ion concentration on the adsorption of plant food by soil colloids. Soil Sci. 14:449–57.

46. Teakle, L. J. H.
1928. Phosphate in the soil solution as affected by reaction and cation concentrations. Soil Sci. **25**:143–62.

47. Tiulin, A. F.
1935. Critical zones of absorbed ions and their availability for plant life. Internatl. Soc. Soil Sci. Trans., Soviet section, vol. A, p. 70–78.

48. Truog, E.
1916. The utilization of phosphates by agricultural crops, including a new theory regarding the feeding power of plants. Wisconsin Agr. Exp. Sta. Research Bul. **41**:1–50.

49. Weiser, V. L.
1933. Fixation and penetration of phosphates in Vermont soils. Vermont Agr. Exp. Sta. Bul. **356**:1–31.

50. Whitson, A. R., and C. W. Stoddard.
1909. Factors influencing the phosphate content of soils. Wisconsin Agr. Exp. Sta. Research Bul. **2**:41–60.

51. Wiley, R. C., and N. E. Gordon.
1923. Availability of adsorbed phosphorus. Soil Sci. **15**:371–72.